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CHEMISTRY

INORGANIC AND ORGANIC

BY THE SAME AUTHOR.

LABORATORY TEACHING;

OR,

PROGRESSIVE EXERCISES IN PRACTICAL CHEMISTRY.

Fifth Edition, with 89 *Engravings, crown* 8*vo.*

CHEMISTRY

INORGANIC AND ORGANIC

WITH EXPERIMENTS

BY

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SIXTH EDITION

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PREFACE.

The Sixth Edition of this work has been carefully revised, and a large part of it has been re-written in order that it may give a more comprehensive view of the Chemistry of the day.

This was particularly necessary in the Organic Chemistry, since the method pursued in earlier editions, of discussing the composition and properties of bodies as they presented themselves in the description of industrial processes, rendered it difficult to give enough attention to their theoretical relations. The treatment adopted in this edition has been to describe the composition, preparation, and properties of the chief members of the great divisions of organic bodies, such as Hydrocarbons, Alcohols, and Acids, giving, where possible, the rational formula, so as to exhibit the relations existing between the groups and between the different members of each group, particular attention being directed to the practical applications of the compounds.

The technological applications of the principles of Organic Chemistry are then described, as in former editions, avoiding repetition of any part of the earlier sections, unless it is absolutely necessary to render the description intelligible, the intention being to bring this part of the subject within the grasp of those who have no interest in the purely theoretical relationships of organic substances.

The work concludes with a consideration of the constitution of the molecules of organic bodies, and of some of the methods adopted for the purpose of obtaining an insight into this, which is essential to the realisation of the highest aspiration of chemists, the complete synthesis of all chemical compounds.

The chief alteration in the Inorganic Chemistry is the introduction of a more systematic description of the individual salts of the metals.

To facilitate laboratory work, weights and measures have been generally given both in English and Continental units, and temperatures have been expressed on the Centigrade scale.

The first edition having appeared when Metallurgy was still treated as a branch of Chemistry, more space is devoted to it than is usual in modern chemical works.

The author's engagements at Woolwich will account for the considerable space allotted to the Chemistry of the various substances employed in warlike stores.

Much assistance has been afforded, in the Organic Chemistry, by Watts' Dictionary, Hodgkinson and Greenaway's translation of Strecker and Wislicenus, and Roscoe and Schorlemmer, especially the volume devoted to the phenyl group.

King's College, London.

PUBLISHERS' NOTE.

It is with deep regret that it falls to us to record here the death, on the 28th ult., of the Author of this work. The association of our Firm with Professor Bloxam had existed for more than thirty-four years, and it is much to our sorrow that one whom we most highly esteemed has thus passed away.

It is no slight satisfaction to us that it is not necessary to add another name to the title-page of this edition. The whole had passed through the press under Professor Bloxam's own hand before he was seized with his fatal illness.

London, *December* 1887.

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ERRATA.

Page 122, l. 15 from foot, *for* "$3H_2$" ***read*** "$3H_2O$."
,, 144, l. 4 from foot, *for* "NO_2" ***read*** "NO."
,, 211, l. 29, *for* "smaller proportion" ***read*** "weaker solution."
,, ,, change the places of the equations in lines 27 and 31.
,, 487, l. 8 from foot, *for* "swcat" ***read*** "sweet."

ATOMIC WEIGHTS.*

Aluminium	Al'''	27	Mercury	Hg' *or* Hg''	200
Antimony	Sb''' *or* Sb^{v}	120	Molybdenum	Mo^{vi}	96
Arsenic	$'''$ or As^{v}	75	Nickel	Ni'' *or* Ni'''	59
Barium	Ba''	137	Niobium	Nb^{v}	94
Bismuth	Bi''' *or* Bi^{v}	208	Nitrogen	N''' *or* N^{v}	14
Boron	B'''	10.9	Osmium	Os^{vi}	200
Bromine	Br'	80	Oxygen	O''	16
Cadmium	Cd''	112	Palladium	Pd'' *or* Pd^{iv}	105.7
Cæsium	Cs'	133	Phosphorus	P''' *or* P^{v}	31
Calcium	Ca''	40	Platinum	Pt'' *or* Pt^{iv}	197.1
Carbon	C^{iv}	12	Potassium	K'	39.1
Cerium	Ce''	140.5	Rhodium	Ro'''	104.3
Chlorine	Cl'	35.5	Rubidium	Rb'	85.3
Chromium	Cr''' *or* Cr^{vi}	52.5	Ruthenium	Ru^{iv}	104.2
Cobalt	Co'' *or* Co'''	59	Samarium	Sm	149.8
Copper	Cu' *or* Cu''	63.5	Scandium	Sc	44
Davyum	Da	154	Selenium	Se''	79.5
Didymium	Di''	144.8	Silicon	Si^{iv}	28.3
Erbium	E''	165.9	Silver	Ag'	108
Fluorine	F'	19	Sodium	Na'	23
Gallium	Ga'''	69.8	Strontium	Sr''	87.5
Germanium	Ge	72	Sulphur	S''	32
Glucinum	G''	9.2	Tantalum	Ta^{iv}	182
Gold	Au'''	196.8	Tellurium	Te''	128
Hydrogen	H'	1	Thallium	Tl'	203.6
Indium	In'''	113.4	Thorium	Th''	232
Iodine	I'	127	Tin	Sn'' *or* Sn^{iv}	118
Iridium	Ir^{iv}	192.5	Titanium	Ti^{iv}	48
Iron	Fe'' *or* Fe'''	56	Tungsten	W^{vi}	184
Lanthanium	La''	139	Uranium	U'' *or* U'''	120
Lead	Pb''	207	Vanadium	V''' *or* V^{v}	51.3
Lithium	L'	7	Yttrium	Y''	89.8
Magnesium	Mg''	24.3	Zinc	Zn''	65.5
Manganese	Mn'' *or* Mn^{iv}	55	Zirconium	Zr^{iv}	90

---

* The accent or index affixed to each symbol expresses the number of atoms of hydrogen for which the atomic weight of the element is *usually* exchangeable in chemical combinations.

The numbers given are not always the results of the exact determinations of atomic weights, but those near approximations to them which are more easily retained in the memory, and are sufficiently accurate for all ordinary calculations, thus, oxygen is given as 16 instead of 15·96.

INTRODUCTION.

MOLECULES AND ATOMS.

CHEMISTRY investigates and compares the properties of all the various kinds of matter, and endeavours to account for the difference in these properties. In order to do this it seeks to comprehend the relations between the ultimate particles or *atoms* of matter which are incapable of further subdivision.

Matter, in a chemical sense, is anything which possesses weight.

The finest state of division of matter with which we are acquainted is that of *gas*, the particles of which are so minute as to be invisible, so that on looking at a glass vessel filled with air or any other colourless gas, it is impossible to say whether it contains any matter or is perfectly empty, that is, a *vacuum*. The doubt may be resolved by heating the vessel, which would have no effect upon a vacuum, but would cause the gas to expand and to exert a greater pressure than before. This expansion of the gas proves that it consists of a number of particles which separate to a greater distance from each other when they are heated. These particles are called *molecules*.*

MOLECULES (*First definition*); the smallest physical particles of matter.

(*Second definition*); those particles of matter which may be removed to a greater distance from each other by the action of heat, without changing the identity of the matter.

If a definite volume of gas be measured at the temperature of melting ice (0° C.), and be then heated to a temperature of 273° C. and again measured, it is found to occupy twice as much space as before, showing that its molecules have been removed to twice the original distance from each other, for the diameters of the molecules are extremely small in comparison with the spaces between them.

A cubic centimetre (about $\frac{1}{16}$th cubic inch) of air is found by calculation to contain 21 trillions of molecules, and these occupy only $\frac{1}{3000}$th part of the entire space; therefore, the sum of the spaces between the molecules is nearly three thousand times as great as the sum of the molecules themselves.

This doubling of the volume happens in the case of every gas, so long as its identity remains unchanged. Since this similarity in expansion by rise of temperature is observed for all temperatures, it is inferred that *equal volumes of all gases at the same temperature contain the same number of molecules.* This is commonly referred to as the *Law of Avogadro.*

---

* Diminutive, from *moles*, a mass.

In the study of physical changes, a molecule, being the smallest physical particle of matter, may be taken as occupying unit of volume, but this would not be convenient in chemistry, as will appear from the following considerations.

If a definite volume of *hydrogen* gas measured at 0° C. be raised to a higher temperature, its increased volume can always be calculated by adding to the volume at 0° as many times $\frac{1}{273}$rd of that volume as there are degrees above 0°, since it suffers a regular expansion of $\frac{1}{273}$rd of its bulk at 0° for each rise of 1° in temperature.

But if a definite volume of *steam* be raised to a *very high* temperature, its volume is found to become half as large again as that of the hydrogen at the same temperature. For the steam has undergone a change in identity, having suffered a chemical decomposition into hydrogen and oxygen, and the volume of the hydrogen is twice that of the oxygen.

Hence, if one volume of steam be raised to a very high temperature, it becomes one volume of hydrogen and half a volume of oxygen.

If a molecule be taken as one volume, it would appear that one molecule of steam is decomposed into one molecule of hydrogen and half a molecule of oxygen.

It appears, then, that when the identity of a gas is changed, some of its molecules are halved; these half molecules are called *atoms.* There is no indication of the possibility of any further division.

Atom (*First definition*); the smallest imaginable particle of matter.

It is evidently convenient to adopt this as the chemical unit of matter, since it is not susceptible of any further change.

(*Second definition of an atom*); that quantity of matter, in the state of gas, which occupies one volume.

Since the half molecules are called atoms, we can give a *third definition of a molecule* as that quantity of matter in the state of gas which occupies two volumes.

The action of a very high temperature upon steam, therefore, is to resolve or decompose two volumes or one molecule of steam into two volumes or atoms of hydrogen and one volume or atom of oxygen.

But the hydrogen and oxygen are in the condition of atoms only at the moment of separation from each other; if they are subsequently examined, they present the ordinary physical properties of gases, showing that they are composed of molecules. Hence atoms have no permanent existence in a separate state, but are always united to form molecules. Indeed, since a molecule is the physical unit of matter, a half molecule would be a physical impossibility; an atom, therefore, is a metaphysical conception.

(*Fourth definition of a molecule*); the smallest quantity of matter which is capable of a separate existence.

(*Third definition of an atom*); the smallest quantity of matter which is capable of existing in a molecule.

It is customary to select hydrogen as the standard chemical unit with which all atoms and molecules are compared. This selection is justified by the consideration that hydrogen is the lightest substance known, so that a very small weight of hydrogen admits of very accurate measurement, and the weights of the molecules of all other bodies are multiples of that of hydrogen.

STANDARD WEIGHTS AND VOLUMES.

The *unit of weight* now very generally adopted by scientific chemists is *one gramme of hydrogen,* which *measures* 11.16 *litres at* 0° *C. and* 760 *mm. Bar.*

Hence, the *unit of volume* is 11.16 *litres.* Since the weight of an atom represents the weight of one volume of a gas (by the second definition of an atom), it is evident that the relative weights of the atoms of different gases may be found by comparing the weights of equal volumes; *e.g.,*

11.16 litres of				Atomic weight.
Hydrogen	weigh	1	grm.	1
Oxygen	,,	16	,,	16
Nitrogen	,,	14	,,	14
Chlorine	,,	35.5	,,	35.5

The relative weights of the molecules are obtained in a similar way, but they are referred to 2 as representing the standard molecular weight of hydrogen (by the third definition of molecule); *e.g.,*

11.16 × 2 litres of				Molecular weight.
Hydrogen	weigh	2	grms.	2
Oxygen	,,	32	,,	32
Water-vapour	,,	18	,,	18
Nitrogen	,,	28	,,	28
Ammonia	,,	17	,,	17
Chlorine	,,	71	,,	71
Hydrochloric acid	,,	36.5	,,	36.5

Definition of atomic weight.—The number of grammes of a simple or elementary substance which occupy 11.16 litres in the state of gas at 0° C. and 760 mm. Bar.

Definition of molecular weight.—The number of grammes of any substance which occupy 22.32 litres in the state of gas at 0° C. and 760 mm. Bar.

Those molecules which are composed of atoms of the same kind are termed *Elements;* those which contain atoms of different kinds are *Compounds.* The greater number of the 71 elements at present known to exist have not yet been measured in the state of gas, so that their relative atomic weights have not been determined in the manner stated above.

But in such cases, some compound which contains the element may be obtained in the form of gas, and from this the relative atomic weight may be found.

Second definition of atomic weight.—The smallest weight of an element which can be found in two volumes (22.32 litres) of any of its gaseous compounds.

Thus carbon has never been measured in the state of vapour, but its atomic weight is inferred to be 12 times that of hydrogen, because no less than 12 grammes of carbon are contained in 22.32 litres of any of the numerous gases formed by the combination of carbon with other elements.

In the rare cases in which no gaseous compound of the element is known, the atomic weight is inferred on the grounds of chemical analogy, or it is ascertained from the specific heat of the element.

The elements known at present are 71 in number, and are divided into metallic and non-metallic elements.

CLASSIFICATION OF THE ELEMENTS.

The *Non-Metallic Elements* are (15).

Oxygen.	Sulphur.	Fluorine.
Hydrogen.	Selenium.	Chlorine.
Nitrogen.	Tellurium.	Bromine.
Carbon.	Phosphorus.	Iodine.
Boron.	Arsenic.*	
Silicon.		

The *Metals* are (56).

Cæsium.	Aluminium.	Zinc.	Copper.	Mercury.
Rubidium.	Gallium.	Nickel.	Bismuth.	Silver.
Potassium.	Germanium.	Cobalt.	Lead.	Gold.
Sodium.	Glucinum.	Iron.	Thallium.	Platinum.
Lithium.	Zirconium.	Manganese.	Tin.	Palladium.
Barium.	Thorium.	Chromium.	Titanium.	Rhodium.
Strontium.	Yttrium.	Cadmium.	Tantalum.	Ruthenium.
Calcium.	Erbium.	Uranium.	Molybdenum.	Osmium.
Magnesium.	Terbium.	Indium.	Tungsten.	Iridium.
	Philippium.		Vanadium.	
	Decipium.		Antimony.	
	Samarium.			
	Ytterbium.			
	Scandium.			
	Cerium.			
	Lanthanum.			
	Didymium.			
	Niobium.			

The strict definition of a metal will be given hereafter.

Many of these elements are so rarely met with, that they have not received any useful application, and are interesting only to the professional chemist. This is the case with selenium† and tellurium, among the non-metallic elements, and with a large number of the metals.

The following list includes those elements with which it is important that the general student should become familiar, together with the symbolic letters by which it is customary to represent them, for the sake of brevity, in chemical writings:—

---

* In many English chemical works arsenic is classed among the metals, which it resembles in some of its properties.

† The remarkable electrical relations of selenium have led to some recent useful applications.

Non-Metallic Elements of practical importance (13).

Oxygen,	O	Sulphur,	S	Fluorine,	F
Hydrogen,	H	Phosphorus,	P	Chlorine,	Cl
Nitrogen,	N	Arsenic,	As	Bromine,	Br
Carbon,	C			Iodine,	I
Boron,	B				
Silicon,	Si				

Metallic Elements of practical importance (26).

Potassium,	K	(*Kalium*)	Cadmium,	Cd	
Sodium,	Na	(*Natrium*)	Uranium,	U	
Barium,	Ba		Copper,	Cu	(*Cuprum*)
Strontium,	Sr		Bismuth,	Bi	
Calcium,	Ca		Lead,	Pb	(*Plumbum*)
Magnesium,	Mg		Tin,	Sn	(*Stannum*)
Aluminium,	Al		Titanium,	Ti	
Zinc,	Zn		Tungsten,	W	(*Wolframium*)
Nickel,	Ni		Antimony,	Sb	(*Stibium*)
Cobalt,	Co		Mercury,	Hg	(*Hydrargyrum*)
Iron,	Fe	(*Ferrum*)	Silver,	Ag	(*Argentum*)
Manganese,	Mn		Gold,	Au	(*Aurum*)
Chromium,	Cr		Platinum,	Pt	

Although the 39 elements here enumerated are of practical importance, many of them derive their importance solely from their having met with useful applications in the arts. The number of elements known to play an important part in the chemical changes concerned in the maintenance of animal and vegetable life is very limited.

Elements concerned in the Chemical Changes taking place in Life.

Non-Metallic.		*Metallic.*	
Oxygen.	Sulphur.	Potassium.	Aluminium.
Hydrogen.	Phosphorus.	Sodium.	Iron.
Nitrogen.	Chlorine.	Calcium.	Manganese.
Carbon.	Iodine.	Magnesium.	
Silicon.			

These elements will, of course, possess the greatest importance for those who study Chemistry as a branch of general education, since a knowledge of their properties is essential for the explanation of the simplest chemical changes which are daily witnessed.

The student who takes an interest in the useful arts will also acquaint himself with the remainder of the 39 elements of practical importance, whilst the mineralogist and professional chemist must extend his studies to every known element.

By far the greater proportion of the various materials supplied to us by animals and vegetables consists of the four elements—oxygen, hydrogen, nitrogen, and carbon; and if we add to these the two most abundant elements in the mineral world, silicon and aluminium, we have the six elements composing the bulk of all matter.

CHEMICAL SYMBOLS.

The symbols of the chemical elements represent their atomic weights: thus H represents one part by weight of hydrogen, O represents 16 parts by weight of oxygen, and C represents 12 parts by weight of carbon. Each symbol therefore represents one volume of the element in the gaseous state.

The molecules (or two gaseous volumes) are represented, as a rule, by writing the figure 2 below and to the right of the symbol: thus H_2 represents a molecule or two parts by weight, or two volumes, of hydrogen; O_2 = a molecule or 32 parts by weight, or two volumes, of oxygen.

The mere contact or mixture of substances is expressed by the sign +; thus $H_2 + Cl_2$ would imply that a molecule of hydrogen had been brought into contact with a molecule of chlorine.

CHEMICAL COMBINATION AND DECOMPOSITION.

Chemical Attraction is the force which holds the atoms of a molecule together. *Chemical Combination* is the exchange of atoms in one molecule for those in another, by which some new kind of matter is produced. For example, chemical combination takes place between hydrogen and chlorine, to form hydrochloric acid, the change being represented by the *chemical equation* $H_2 + Cl_2 = 2HCl$, which implies that the molecules of hydrogen and chlorine exchange atoms.

It will be seen from the statements made above, that this equation also implies that 2 parts by weight of hydrogen and 35.5 × 2 parts by weight of chlorine, yield 36.5 × 2 parts by weight of hydrochloric acid.

The equation also informs us that 2 volumes of hydrogen and 2 volumes of chlorine would combine to form 4 volumes of hydrochloric acid.

It must be remembered that a chemical equation is only a short mode of expressing the result of an experiment, and cannot be used like a mathematical equation, to effect the solution of a problem.

A chemical equation may be written to express what is likely to result from the action of different molecules upon each other, but it has no value until verified by experiment.

Chemical Decomposition is the separation of the atoms composing a molecule, which must precede the formation of a new molecule. Thus, the decomposition of steam by a very high temperature is expressed by the equation $2H_2O = 2H_2 + O_2$, which conveys the information that two molecules or 4 volumes or 36 parts by weight of steam, have suffered chemical decomposition, and have formed two molecules or 4 volumes or 4 parts by weight of hydrogen, and one molecule or 2 volumes or 32 parts by weight of oxygen.

Chemical changes are always attended by evolution or absorption of heat. As a general rule, the formation of compound molecules from elementary molecules evolves heat, whilst the formation of elementary molecules from compound molecules absorbs heat. Hence it will be found that the application of heat is generally required for the commencement of chemical change, in order to effect that separation of atoms from their molecules which must precede every chemical transformation of matter. When any chemical change appears to take place without any change of temperature being observed, it is because the total heat absorbed in the destruction of the original molecules is equal to the total heat evolved in the construction of the new molecules.

The formation of water by the chemical combination of hydrogen and oxygen consists in the separation of the atoms which compose the oxygen molecule, and of those composing two hydrogen molecules, an atom of hydrogen from each hydrogen molecule uniting with an atom of oxygen from the oxygen molecule, as expressed in the equation, $OO + \mathrm{H}H + \mathrm{H}H = \mathrm{HHO} + HHO$. Here, it is evident that the conversion of a molecule of oxygen into water is effected by the exchange of each of its oxygen atoms for two hydrogen atoms.

Since hydrogen is taken as the chemical standard or unit, and one atom of oxygen is exchangeable for two atoms of hydrogen, oxygen is said to be *divalent* or *diad*, often expressed by writing it thus, O''. The atoms of some elements are exchangeable for three atoms of hydrogen, and are said to be *trivalent* or *triad* $'''$; others for four, *quadrivalent* or *tetrad* $^{\mathrm{iv}}$, or for five, *quinquivalent* or *pentad* $^{\mathrm{v}}$, and so on.

A convenient classification is thus arrived at, which is liable, however, to a great number of exceptions.

Monads—Br, Cl, F, I, K, Ag, Na.

Diads—Ba, Cd, Ca, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, O, Sr, S, Zn.

Triads—Al, Sb, As, Bi, B, Cr, Au, N, P.

Tetrads—C, Pt, Si, Sn.

CLASSIFICATION OF COMPOUNDS.

Compound substances are commonly classified by the chemist into *Organic* and *Inorganic* compounds; and although it is impossible strictly to define the limits of each class, the division is a convenient one for the purposes of study.

Organic substances may be defined as those for which we are indebted to the operation of animal or vegetable life, such as starch, sugar, &c.

Inorganic substances are obtained from the mineral world without the intervention of life; as common salt, alum, &c.

Organic substances always contain carbon, generally also hydrogen and oxygen, and very frequently nitrogen.

OBJECT OF CHEMISTRY.

It is the object of Chemistry (1) so to study the properties of a body as to be able to identify it with certainty under whatever conditions it may be met with, (2) to find a method of making it at pleasure, (3) to discover its exact composition, by weight and by volume, (4) to examine its action upon other substances in order to ascertain its chemical constitution.

PHYSICAL AND CHEMICAL PROPERTIES.

In studying the properties of bodies, a distinction must be drawn between physical and chemical properties. The physical properties are those in which either the *mass* or the *molecules* only are concerned, while the chemical properties concern the *atoms*. Thus, the condition, whether solid, liquid, or gas, the colour, odour, taste, hardness, relative weight (or specific gravity), would come under the head of physical properties. For a solid, the geometrical form of its crystal and the temperature at which it melts are important for identification, and for a liquid, the temperature at which it boils.

INORGANIC CHEMISTRY.

CHEMISTRY OF THE NON-METALLIC ELEMENTS AND THEIR COMPOUNDS.

THE ELEMENTS OF WATER.

1. A century has but just elapsed since water ceased to be regarded as an elementary form of matter. It was first resolved into its constituent elements, hydrogen and oxygen, by subjecting it to the influence of the *voltaic current*, which decomposes or *analyses* the water by overcoming the chemical attraction by which its elements are held together.

An arrangement for this purpose is represented in fig. 1.

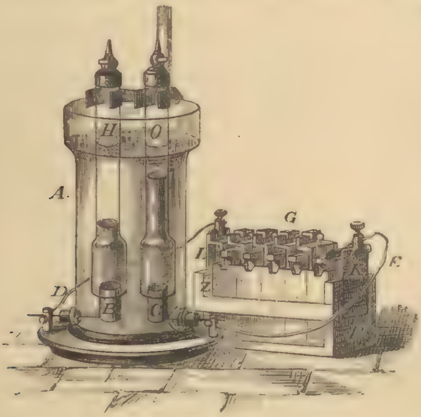

Fig. 1.—Electrolysis of water.

The glass vessel **A** contains water, to which a little sulphuric acid has been added to increase its power of conducting electricity, for pure water conducts so imperfectly that it is decomposed with great difficulty. B and C are platinum plates bent into a cylindrical form, and attached to the stout platinum wires, which are passed through corks in the lateral necks of the vessel A, and are connected by binding screws with the copper wires D and E, which proceed from the galvanic battery G. H and O are glass cylinders with brass (or glass) caps and stop-cocks, and are enlarged into a bell-shape at their lower ends for the collection of a considerable volume of gas. These cylinders are filled with the acidulated water by sucking out the air through the opened stop-cocks; on closing these, the pressure of the air will, of course, sustain the column of water in the cylinders. G is a Grove's battery, consisting of five cells or earthenware vessels (A, fig. 2) filled with diluted sulphuric acid (one measure of oil of vitriol to four of water). In each of these cells is placed a bent plate of zinc (B), which has been *amalgamated* or rubbed with mercury (and diluted sulphuric acid) to protect it from corrosion by the acid when the battery is not in use. Within the curved portion of this plate rests a small flat vessel of unglazed earthenware (C), filled with strong nitric acid, in which is immersed a sheet of platinum foil (D). The platinum (D) of each cell is clamped, at its upper edge, to the zinc (B) in the adjoining cell (fig. 3), so that at one end (P, fig. 1) of the battery there is a free platinum plate, and at the other (Z) a free zinc plate. These plates are connected with the wires D and E by means of the copper plates L and K, attached to the ends of the wooden trough in which the cells are arranged. The wire D (fig. 1), which is connected with the last *zinc* plate of the battery, is often called the "*negative* pole;" whilst E, in connexion with the last *platinum* plate, is called the "*positive* pole."

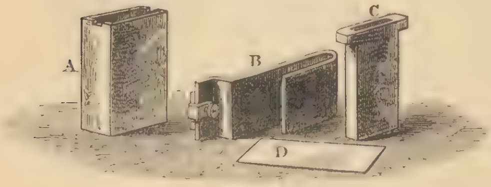

Fig. 2.

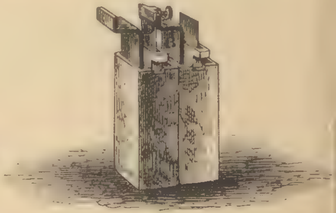

Fig. 3.

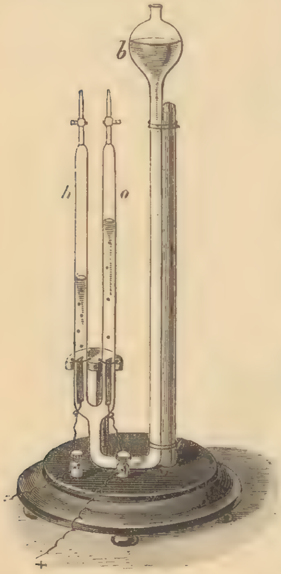

Fig. 4.—Electrolysis of water.

When the connexion is established by means of the wires D and E with the "decomposing cell" (A), the "galvanic current" is commonly said to pass along the wire E to the platinum plate C, through the acidulated water in the decomposing cell, to the platinum plate B, and thence along the wire D back to the battery.

A very elegant apparatus (fig. 4) has been devised by Dr. Hofmann for exhibiting the decomposition of water by the galvanic current. The water displaced by the gases accumulating in the tubes *h*, *o*, collects in the bulb *b* upon the longer branch, and exerts the pressure necessary to force the gases out when the stop-cocks are opened. The stop-cocks, being made of glass, are not corroded by the acid.

2. During this "passage of the current" (which is only a figurative mode of expressing the transfer of the electric influence), the water intervening between the plates B and C is decomposed, its hydrogen being attracted to the plate B (negative pole), and the oxygen to the plate C (positive pole). The gases can be seen adhering in minute bubbles to the surface of each plate, and as they increase in size they detach themselves, rising through the acidulated water in the tubes H and O, in which the two gases are collected.

Since no transmission of gas is observed between the two plates, it is evident that the H and O separated at any given moment from each plate do not result from the decomposition of one particle of water, but from two particles, as represented in fig. 5, where A represents the particles of water lying between the plates P and Z before the "current" is passed, and B the state of the particles when the current has been established. P is (the positive pole) in connexion with the last platinum plate of the battery, and Z is (the negative pole) in connexion with the last zinc plate.

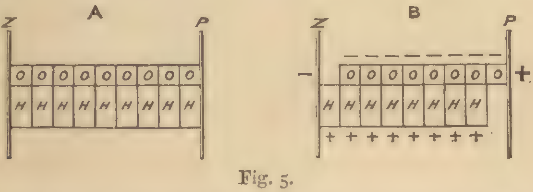

Fig. 5.

The signs + and − made use of in B refer to a common mode of accounting for the decomposition of water by the battery, on the supposition that the oxygen is in a negatively electric condition, and therefore attracted by the positive pole P; whilst the hydrogen is in a positively electric condition, and is attracted by the negative pole Z.

In the foregoing explanation, the part played by the sulphuric acid has been omitted for the sake of simplicity. Pure water could not be decomposed unless by a very much stronger battery. The sulphuric acid H_2SO_4 is first decomposed, the H_2 being attracted to the negative pole, and the O to the positive pole, while the SO_3, combining with more H_2O, forms H_2SO_4, which is in its turn decomposed by the current; hence a very little sulphuric acid enables a large quantity of water to be decomposed.

The decomposition of compounds by galvanic electricity is termed *electrolysis*.* When a compound of a metal with a non-metal is decomposed in this manner, the metal is usually attracted to the (negative) pole in connexion with the zinc plate of the battery, whilst the non-metal is attracted to the (positive) pole connected with the platinum plate of the battery.

Hence the metals are frequently spoken of as *electro-positive* elements, and the non-metals as *electro-negative*.

3. If the passage of the "current" be interrupted when the tube H has become full of gas, the tube O will be only half full, since *water contains hydrogen and oxygen in the proportion of two volumes of hydrogen to one volume of oxygen*. When the wider portions of the tubes (fig. 1) are also filled, the two gases may be distinguished by opening the stop-cocks in succession, and presenting a burning match. The hydrogen will be known by its kindling with a slight detonation, and burning with a very pale flame at the jet; whilst the oxygen will very much increase the brilliancy of the burning match, and if a spark left at the extremity of the match be presented to the oxygen, the spark will be kindled into a flame.

Another method of effecting the decomposition of water by electricity consists in passing a succession of electric sparks through steam. It is probable that in this case the decomposition is produced rather by the intense heat of the spark than by its electric influence.

For this purpose, however, the galvanic battery does not suffice, since no spark can be passed through any appreciable interval between the wires of the battery,—a fact which electricians refer to in the statement that although the *quantity* of electricity developed by the galvanic battery is large, its *tension* is too low to allow it to discharge itself in sparks like the electricity from the machine or from the induction-coil, which possesses a very high tension, though its quantity is small.

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* Ἤλεκτρον, amber—root of *electricity*; λύω, to loosen.

4. The most convenient instrument for producing a succession of electric sparks is the *induction-coil*, in which a current of low tension, sent from a weak battery through a coil of stout wire and back to the battery, induces or excites a current of high tension in a coil of thin wire of great length, wound outside the thick coil. This current is capable of discharging itself in sparks, such as are obtained from the electrical machine.

Fig. 6 represents the arrangement for exhibiting the decomposition of steam by the electric spark.

A is a half-pint flask furnished with a cork in which three holes are bored; in one of these is inserted the bent glass tube B, which dips beneath the surface of the water in the trough C.

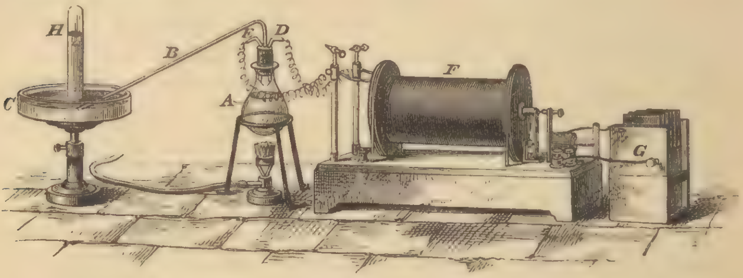

Fig. 6.—Decomposition of steam by electric sparks.

D and E are glass tubes, in each of which a platinum wire has been sealed so as to project about an inch at both ends of the tube. These tubes are thrust through the holes in the cork, and the wires projecting inside the flask are made to approach to within about $\frac{1}{16}$th of an inch, so that the spark may easily pass between them.

The flask is somewhat more than half filled with water, the cork inserted, and the tube B allowed to dip beneath the water in the trough, the wires in D and E being connected with the thin copper wires passing from the induction-coil F, which is connected by stout copper wires with the small battery G.

The water in the flask is boiled for about fifteen minutes, until all the air contained in the flask has been displaced by steam. When this is the case, it will be found that if a glass test-tube (H) filled with water be inverted* over the orifice of the tube B, the bubbles of steam will entirely condense, with the usual sharp rattling sound, and only insignificant bubbles of air will rise to the top of the test-tube. If now, whilst the boiling is still continued, the handle of the coil (F) be turned so as to cause a succession of sparks to pass through the steam in the flask, large bubbles of incondensable gas will accumulate in the tube H. This gas consists of the hydrogen and oxygen gases in a *mixed* state, having been released from their *combined* condition in water by the action of the electric sparks. The gas may be tested by closing the mouth of the tube H with the thumb, raising it to an upright position, and applying a lighted match, when a sharp detonation will indicate the recombination of the gases.†

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* The end of the tube B should be bent upwards and thrust into a perforated cork with notches cut down the sides. By slipping this cork into the neck of the test-tube, the latter will be held firmly.

† With a powerful coil, a cubic inch of explosive gas may be collected in about fifteen minutes.

It has long been known that a very intense heat is capable of decomposing water. The temperature required for the purpose is below the melting point of platinum, as may be shown by the apparatus represented in fig. 7.

A platinum tube (*t*) is heated by the burner *b*, the construction of which is shown at the bottom of the cut. It consists of a wide brass tube, from which the coal-gas issues through two rows of holes, between which oxygen is supplied through the holes in the narrow tube, brazed into a longitudinal slit between the two rows of holes in the gas tube. The oxygen is supplied from a gas bag or gas-holder, with which the pipe (*o*) is connected.

The flask (*f*) containing boiling water is furnished with a perforated cork, carrying a brass tube (*a*), which slips into one end of the platinum tube, into the other end of which another brass tube (*c*) is slipped; this is prolonged by a glass tube attached by india-rubber, so as to deliver the gas under a small jar standing upon a bee-hive shelf in a trough.

The platinum tube is not heated until the whole apparatus is full of steam, and no more bubbles of air are seen to rise through the water in the trough; the gas burner is then lighted, and the oxygen turned on until the platinum tube is heated to a very bright red heat; bubbles of the mixture of hydrogen and oxygen resulting from the decomposition of the water may then be collected in the small jar, and afterwards exploded by applying a flame.

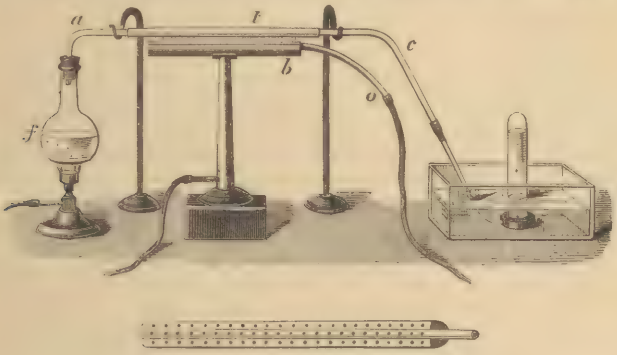

Fig. 7.—Decomposition of steam by heat.

In these experiments, the high temperature to which the steam is exposed causes its molecules to vibrate with such high velocities that the equilibrium of chemical forces in their component atoms is disturbed, and new molecules of hydrogen and oxygen are produced. These are immediately carried out of the heated region by the current of steam.

5. In this case, the force of chemical attraction holding the atoms of oxygen and hydrogen together in the form of water, has been overcome by the physical force of heat. But water may be more easily decomposed by acting upon it with some element which has sufficient chemical energy to enable it to displace the hydrogen.

No non-metallic element is capable of effecting this at the ordinary temperature. Among the practically important metals, there are five which have so powerful an attraction for oxygen that it is necessary to preserve them in bottles filled with some liquid free from that element, such as petroleum (composed of carbon and hydrogen), to prevent them from combining with the oxygen of the atmosphere. These metals are capable of decomposing water with great facility.

Metals which decompose water at the ordinary temperature.—Potassium, Sodium, Barium, Strontium, Calcium.

6. When a piece of potassium is thrown upon water, it takes fire and

burns with a fine violet flame, floating about as a melted globule upon the surface of the water, and producing in the act of combination enough heat to kindle the hydrogen as it escapes. The violet colour of the flame is due to the presence of a little potassium in the form of vapour. The same results ensue if the potassium be placed on ice. The water in which the potassium has been dissolved will be found soapy to the touch and taste, and will have a remarkable action upon certain colouring matters. Paper coloured with the yellow dye *turmeric* becomes brown when dipped in it, and paper coloured with *red litmus* (*archil*) becomes blue. Substances possessing these properties have been known from a very remote period as *alkaline* substances, apparently because they were first observed by the alchemists in the ashes of plants called *kali*. The alkalies are amongst the most useful of chemical agents.

7. *Definition of an alkali.*—A compound substance, very soluble in water, turning litmus blue and turmeric brown.

These alkaline properties are directly opposed to the characters of sour or *acid*[*] substances, such as vinegar or vitriol, which change the blue litmus to red. When an acid liquid such as vinegar (acetic acid) or vitriol (sulphuric acid) is added to an alkaline liquid, the characteristic properties of the latter are destroyed, the alkali being *neutralised*.

An acid substance may be known by its property of neutralising an alkali (either entirely or partly).

The minute investigation into the action of potassium upon the water would require considerable manipulative skill. It would be necessary to weigh accurately the potassium employed, to evaporate the resulting solution in a silver basin (most other materials being corroded by the alkali), and after all the water had been expelled by heat, to ascertain the composition of the residue by a chemical analysis.

It would be found to contain by weight 1 part of hydrogen, 16 parts of oxygen, and 39.1 parts of potassium.

Since water contains 2 parts by weight of hydrogen, combined with 16 parts of oxygen, it is evident that the product of the action of potassium on water is formed by the substitution of 39.1 parts of potassium for 1 part of hydrogen.

It is found that whenever potassium takes the place of hydrogen in a compound, 39.1 parts of the former are exchanged for one of the latter, and this is generally expressed by stating that 39.1 is the *chemical equivalent* of potassium.

The *chemical equivalent of a metal* expresses the weight which is required to be substituted for one part by weight of hydrogen in its compounds.

8. The action of potassium upon water is an example of the production of compounds by substitution of one element for another, a mode of formation which is far more common than the production of compounds by direct combination of their elements.

If the symbol K be taken to represent 39.1 parts by weight of potassium, its action upon water would be represented by the chemical equation

$$\underset{\text{Water.}}{H_2O} + K = \underset{\text{Caustic potash.}\dagger}{KOH} + H.$$

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[*] From ἀκή, a point, referring to the pungency or sharpness of the acid taste.

[†] Caustic, from καίω, to burn, in allusion to its corrosive properties; and potash, from its having been originally prepared from the washings of wood ashes boiled down in iron pots and decomposed by lime.

But since the atoms cannot exist, except in combination as molecules, it would be strictly correct to write the equation thus:

$$2H_2O + K_2 = 2KOH + H_2.$$

Since the molecular equation can, always be obtained by doubling the atomic equation, the latter will be most commonly given in this work, as involving fewer numbers.

Sodium has a less powerful attraction for oxygen than potassium, and does not usually take fire when thrown into cold water, although it is at once fused by the heat evolved. By holding a lighted match over the globule as it swims upon the water, the hydrogen may be kindled, when its flame is bright yellow, from the presence of the sodium. The solution will be found strongly alkaline from the soda produced. By placing the sodium on a piece of blotting paper laid on the water, it may be made to ignite the hydrogen spontaneously, because the paper keeps it stationary, and prevents it from being so rapidly cooled by the water. Several cubic inches of hydrogen may easily be collected by placing a piece of sodium as large as a pea in a small wire-gauze box (A, fig. 8), and holding it under an inverted cylinder (B) filled with water and standing on a bee-hive shelf.*

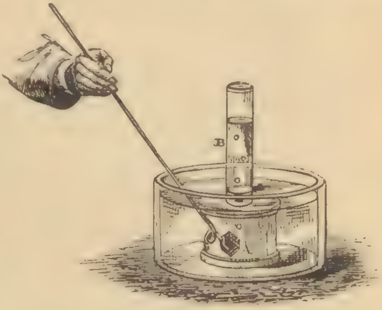

Fig. 8.

The product of the action of sodium upon water contains 1 part by weight of hydrogen, 16 of oxygen, and 23 of sodium, so that the 23 parts of sodium have been exchanged for, or been found chemically equivalent to, 1 part of hydrogen.

Taking the symbol Na to represent 23 parts by weight of sodium, its action would be expressed thus: $H_2O + Na = NaOH + H$.

Barium, strontium, and calcium decompose water less rapidly than potassium and sodium.

9. The increase in molecular motion caused by heat disturbs the equilibrium of chemical forces, so that metals which refuse to decompose water at the ordinary temperature, will do so if the temperature be raised, and accordingly magnesium and manganese, which are without action upon cold water, decompose it *at the boiling point*, disengaging hydrogen, and producing magnesia (MgO, a feebly alkaline earth), and oxide of manganese (MnO).

But the greater number of the common metals must be raised to a much higher temperature than this in order to enable them to decompose water. The following metals will abstract the oxygen from water at high temperatures, those at the commencement of the list requiring to be heated to redness (about 600° C.), and the temperature required progressively increasing until it attains whiteness for those at the end of the list.

Metals which decompose water at a temperature above a red heat.—Zinc, Iron, Chromium, Cobalt, Nickel, Tin, Antimony, Aluminium, Lead, Bismuth, Copper.

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* This experiment sometimes ends in an explosion.

The *noble metals*, as they are called, which exhibit no tendency to oxidise in air, are incapable of removing the oxygen from water, even at high temperatures.

Metals which are incapable of decomposing water.—Mercury, Silver, Gold, Platinum.

Metals decompose water more readily when they are placed in a state of electrical polarisation by contact with other metals more electro-negative than themselves. Thus zinc, in contact with precipitated copper, will decompose water slowly at the ordinary temperature, hydrogen being evolved, and zinc hydrate separated in white flakes.

The *copper-zinc couple* made by precipitating copper sulphate with zinc foil in excess, and washing, is very useful in many operations where a slow production of hydrogen is required.

HYDROGEN.

H = 1 part by weight = 1 vol. 1 grain = 46.7 cub. in. at 60° F. and 30" Bar.
1 gramme = 11.16 litres at 0° C. and 760 mm. Bar.

10. *Preparation of hydrogen.*—The simplest process, chemically speaking, for preparing hydrogen in quantity, consists in passing steam over red-hot iron. An iron tube (A, fig. 9) is filled with iron nails and fixed across a furnace (B), in which it is heated to redness by a charcoal fire. A current of steam is then passed through it by boiling the water in the flask (C), which is connected with the iron tube by a glass tube (D) and perforated corks. The hydrogen is collected from the glass tube (G) in cylinders (E) filled with water, and inverted in the trough (F) upon the bee-hive shelf (H), the first portions being allowed to escape, as containing the air in the apparatus.

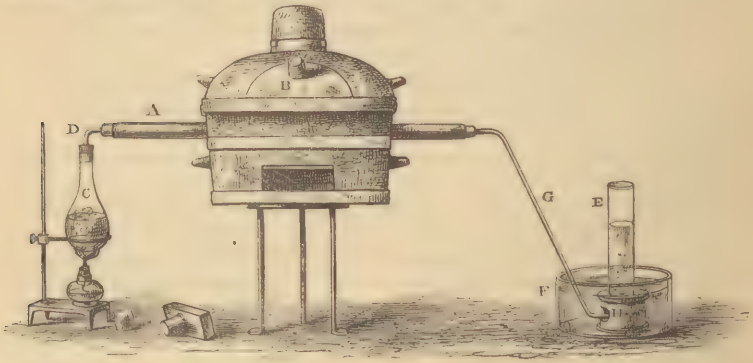

Fig. 9.—Preparation of hydrogen from steam.

The iron combines with the oxygen of the water to form the black oxide of iron (Fe_3O_4) which will be found in a crystalline state upon the surface of the metal. The decomposition is represented by the equation $\underset{\text{Water.}}{4H_2O} + Fe_3 = \underset{\text{Black oxide of iron.}}{Fe_3O_4} + H_8$.

The weight of an atom of iron is 56 times that of an atom of hydrogen; hence the Fe_3 in the above equation represent 56 × 3, or 168 parts by weight of iron.

The process by which hydrogen is most commonly prepared consists in dissolving iron or zinc in a mixture of sulphuric acid and water.

Zinc is the most convenient metal to employ for the preparation of hydrogen in this way It is used either in small fragments or cuttings, or as *granulated zinc*, prepared by melting it in a ladle and pouring it from a height of three or four feet into a pailful of water. The zinc is placed in the bottle (A, fig. 10), covered with water to the depth of two or three inches, and diluted sulphuric acid slowly poured in through the funnel tube (B) until a pretty brisk effervescence is observed. The hydrogen is unable to escape through the funnel tube, since the end of it is beneath the surface of the water, but it passes off through the bent tube (C), and is collected over water as usual, the first portion being rejected as containing air.

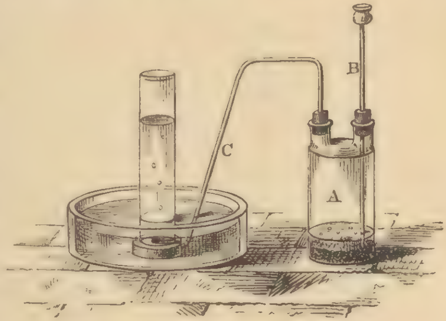

Fig. 10.—Preparation of hydrogen.

By allowing the solution left in the bottle to cool in another vessel, crystals of zinc sulphate (*white vitriol*) may be obtained.

It will be noticed that the liquid becomes very hot during the action of the acid upon the zinc, the heat being produced by the combination which is taking place. The black flakes which separate during the solution of the zinc consist of metallic lead, which is always present in the zinc of commerce, and much accelerates the evolution of hydrogen by causing galvanic action. Pure zinc placed in contact with diluted sulphuric acid evolves hydrogen very slowly.

The preparation of hydrogen by dissolving zinc in diluted sulphuric acid may be represented by the equation [*]

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + Zn = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

The symbol Zn here represents an atom of zinc, which is 65 times as heavy as the atom of hydrogen. An atom of zinc has here displaced 2 atoms of hydrogen, whereas it was found that an atom of potassium displaced only 1 atom of hydrogen, which is often expressed by saying that potassium is a *monatomic* element, *i.e.*, is exchangeable for 1 atom of hydrogen.[†] But since 65 parts of zinc displace 2 parts of hydrogen, zinc is a *diatomic* element, *i.e.*, is exchangeable for 2 atoms of hydrogen. This is commonly expressed by writing the symbol of zinc Zn''.

It may be supposed that the atom of a monatomic element, such as hydrogen or potassium, exerts its chemical attraction in one direction only, as represented by a single line or *bond* attached to the symbol, thus $H-$, $K-$; whilst a diatomic element, such as zinc, exerts chemical attraction in two directions, represented by attaching two lines to the symbol, thus $-Zn-$, or $Zn<$. Since an atom of oxygen combines with two atoms of hydrogen, it must also exert chemical attraction in two directions, so that a molecule of water may be represented as

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[*] In this equation the excess of water which must be added to dissolve the zinc sulphate is not set down. Hydrogen could not be prepared according to the equation as it stands, because the zinc sulphate would collect round the metal and prevent further action.

[†] Zinc is one of the exceptions to the law of volumes; 65 grammes of zinc give 22.32 litres of vapour, so that one atom of zinc represents two volumes.

H--O--H. The displacement of half the hydrogen by potassium (p. 14) then produces K--O--H, caustic potash, and the displacement of both atoms of hydrogen by zinc produces Zn<>O, or zinc and oxygen united by both their *bonds* of chemical attraction, forming zinc oxide.

Iron might be used instead of zinc, and the solution, when evaporated, would then deposit crystals of *green vitriol* or *copperas* (sulphate of iron, or ferrous sulphate, $FeSO_4$), the action of iron upon the sulphuric acid being represented by the equation $\underset{\text{Sulphuric acid.}}{H_2SO_4} + Fe = \underset{\text{Ferrous sulphate.}}{FeSO_4} + H_2$, which shows that 1 atom (56) of iron has taken the place of 2 atoms of hydrogen, and that the iron is diatomic, like zinc.

Hydrogen has been prepared cheaply in large quantity by heating a mixture of slaked lime with anthracite coal in an iron retort; $C + CaO + 2H_2O = CaCO_3 + H_4$. On passing steam over the residue; $CaCO_3 = CaO + CO_2$: hence, if enough carbon be employed in the beginning, large quantities of hydrogen may be obtained by steaming and heating alternately.

11. *Physical properties of hydrogen.*—This gas is invisible, and inodorous when pure. The hydrogen obtained by the ordinary methods has a very disagreeable smell, caused by the presence of minute quantities of compounds of hydrogen with sulphur, arsenic, and carbon; but the gas prepared with pure zinc and sulphuric acid is quite free from smell. It is liquefied with extreme difficulty, requiring a pressure of 650 atmospheres at $-220°$ F. ($-140°$ C.), and yielding a blue liquid. The most remarkable physical property of hydrogen is its lightness. It is the lightest of all kinds of matter, being about $\frac{1}{15}$ as heavy as air, and $\frac{1}{11162}$ as heavy as water.

The lightness of hydrogen may be demonstrated by many interesting experiments. Soap bubbles or small balloons (of *collodion*, for example) will ascend very rapidly if inflated with hydrogen. A light beaker glass may be accurately weighed in a pair of scales; it may then be held with its mouth downwards, and the hydrogen poured up into it from another vessel. If it be then replaced upon the scale-pan with its mouth downwards, it will be found very much lighter than

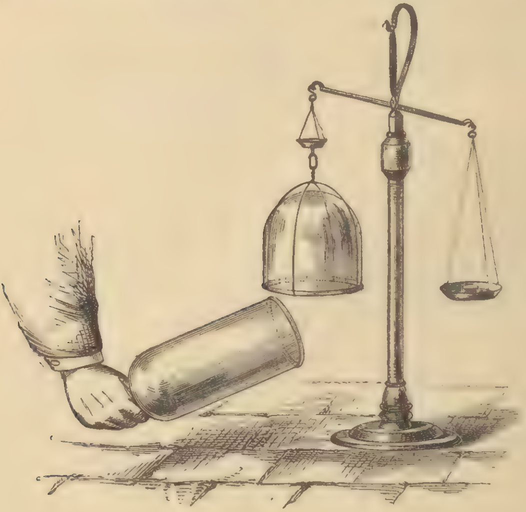

Fig. 11.

before. Another form of the experiment is represented in fig. 11, where a light glass shade has been suspended from the balance and counterpoised, the equilibrium being, of course, at once disturbed when hydrogen is poured up into the shade. If a stoppered gas jar full of hydrogen be held with its mouth downwards, and a piece of smouldering brown paper held under it, the smoke, which would rise freely in the air, is quite unable to rise through the hydrogen, and remains at the mouth of the jar until the stopper is removed, when the hydrogen quickly rises and the smoke follows it.

12. The employment of hydrogen for filling balloons renders a knowledge of the relation between the weights of equal volumes of hydrogen and atmospheric air of great importance. The number expressing this relation is termed the *Specific Gravity* of hydrogen.

(DEFINITION.—The specific gravity of a gas or vapour is its weight as compared with that of an equal volume of some other gas, selected as a standard, at the same temperature and pressure.)

If the weight of a given volume of purified and dried air be represented as unity, an equal volume of hydrogen, at the same temperature and pressure, would weigh 0.0692, which is expressed by saying that the specific gravity of hydrogen (air = 1) is 0.0692.

In ascertaining the weights of definite volumes of gases, it is of the greatest importance that they should have some definite temperature and pressure, since the volume of a given weight of gas is augmented by the increase of temperature and by decrease in pressure. It is usual to state the weights of gases, either at 60° Fahrenheit and 30 inches barometer; or at 0° Centigrade and 760 millimetres barometer.

One grain of hydrogen, at 60° F. and 30 inches Bar., measures 46.73 cubic inches.

One gramme (15.43 grains) of hydrogen, at 0° C. and 760 mm. Bar., measures 11.16 litres (one litre = 61.024 cubic inches = 1.76 pint).

It is now easy to calculate how much zinc it would be necessary to dissolve in sulphuric acid in order to obtain any desired volume, say 100 litres of hydrogen. Referring to the equation for the preparation of hydrogen, $Zn + H_2SO_4 = H_2 + ZnSO_4$. and remembering that Zn represents 65 parts by weight of zinc, and H_2 represent 2 parts by weight of hydrogen—

(2 grms. H) 22.32 litres : 100 litres : : 65 grms. zinc : x.

$x = 291$ grms. zinc give 100 litres of hydrogen at 0° C. and 760 mm. Bar.

13. It will be observed, in the experiment with the balance (fig. 11), that the gas gradually *falls* out of the jar, notwithstanding its lightness, and is replaced by air; so that, after a time, the equilibrium is restored, proving that the molecules of hydrogen possess motion which is independent of gravitation. This is evident also from another consideration. The total weight of the molecules of hydrogen in one cubic centimetre of the gas at 0° C. and 760 mm. Bar. is only .0000896 gramme, and yet its pressure upon the sides of the vessel containing it amounts to 1033 grammes per square centimetre.

The weight of a single molecule of hydrogen has been calculated to be not greater than one ten-thousand-millionth of a gramme,* and 21 trillions of them are calculated to be contained in one cubic centimetre. This enormous number of molecules, moving with great velocity and delivering successive blows on the sides of the vessel, give rise to the pressure of the gas.

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* This has been inferred from the fact that one drop of a solution containing .00000002 gramme of aniline-red presents a distinct red colour. The molecular weight of aniline-red (rosaniline hydrochloride, $C_{20}H_{19}N_3.HCl$) is 337.5 times that of an atom of hydrogen; and since the molecule of aniline-red cannot weigh *more* than .00000002 gramme, the atom of hydrogen cannot weigh more than $\frac{1}{337.5}$ of that quantity, or $10^{-12} \times 59$ grammes, so that the molecule of hydrogen cannot weigh *more* than twice this, or $10^{-12} \times 118$ grammes.

Hence the pressure of a gas will vary with the weight of its molecules, and with their velocity. If m be taken to represent the weight of a molecule, and v its velocity, mv will express the momentum of each molecule; but the pressure depends not only on the momentum of each molecule, but on the number of blows delivered by each molecule in equal times, which will increase with the velocity of the molecule. Hence $mv \times v$ or mv^2 will represent the pressure of the gas. Suppose this pressure to be some constant unit of pressure, represented by 1, then $mv^2 = 1$, and

$$v^2 = \frac{1}{m}, \text{ or } v = \frac{1}{\sqrt{m}},$$

showing that the velocities of the molecules of gases vary inversely as the square roots of their molecular weights. But the molecular weights of the gases represent the weights of equal volumes (see p. 3), or the specific gravities of the gases, so that *the velocities of the molecules of gases vary inversely as the square roots of their specific gravities.*

The absolute velocity of the molecules of a gas may be calculated when the pressure, the temperature, and the weight of a given volume of the gas are known. It has thus been determined that the absolute velocity of a molecule of hydrogen at 0° C. and 760 mm. Bar. is 1859 metres (6050 feet) per second. Oxygen is 16 times as heavy as hydrogen; hence the velocity of the oxygen molecule, for the same temperature and pressure, would be $\frac{1}{\sqrt{16}} = \frac{1}{4}$th that of the hydrogen molecule, or 1512 feet per second.

This view of the constitution of gases (known as the *kinetic* theory, from *κίνησις, motion*) explains their remarkable physical properties. If a vessel of hydrogen at 760 mm. pressure were opened into a vacuum, the molecules of hydrogen would escape into the vacuum with a velocity of 6050 feet per second. If the vessel be opened in air, the velocity of the hydrogen molecules will be retarded by collision with the air molecules, but the gas still escapes very rapidly.

The nitrogen and oxygen gases, which are mixed together in air, being respectively 14 and 16 times as heavy as hydrogen, their molecules have a lower velocity, and are not carried into the vessel so rapidly as the hydrogen passes out. In order to render this evident, the opening of the vessel should be closed by some material having very minute pores, so as to retard the exchange of the gases, and to measure the relative velocities of their molecules, or the *rates of diffusion* of the gases.

The *diffusion tube* (fig. 12) employed for this purpose is a glass tube (A) closed at one end by a plate of plaster of Paris (B). If this tube be filled with hydrogen,* and its open end immersed in coloured water, the water will be observed to rise rapidly in the tube, on account of the rapid escape of the hydrogen through the pores of the plaster. The external air, of course, passes into the tube through the pores at the same time, but much less rapidly than the hydrogen passes out, so that the ascent of the column of water (C) marks the difference between the volume of hydrogen which passes out, and that of air which passes into the tube in a given time, and allows a measurement to be made of the *rate of diffusion;* that is, of the velocity with which the gas issues as compared with the velocity with which the air enters, this velocity being always taken as unity.[*] To determine the rate of diffusion, it is of course necessary to maintain the water at the same level within and without the diffusion tube, so as to exclude the influence of pressure.

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* This tube must be filled by displacement (see fig. 18), in order not to wet the plaster. A piece of sheet caoutchouc may be tied over the plaster of Paris, so that diffusion may not commence until it is removed.

To prove that the ascent of the hydrogen due to its lightness is not instrumental in drawing up the water in the diffusion tube, the experiment may be made as in fig. 13, where the plate of plaster (*o*) is turned downwards, so that the diffusion is made to take place in opposition to the action of gravity. This tube is filled by passing hydrogen in through the tube (*s*), and allowing the air to escape through (*t*), which is afterwards closed by a cork. The plaster of Paris (*o*) is tied over with caoutchouc whilst the tube is filled.

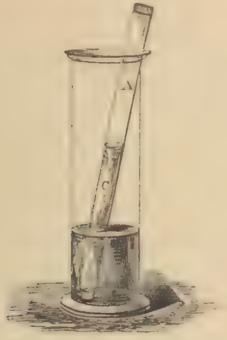

Fig. 12.—Diffusion tube.

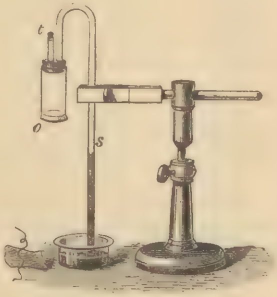

Fig. 13.

Since the relation between the weights of equal volumes of hydrogen and air is that of 0.069 : 1, the rates of diffusion will be as $1 : \sqrt{0.069}$—that is, hydrogen will diffuse about 3.8 times as rapidly as atmospheric air, or 3.8 measures of hydrogen will pass out of the diffusion tube whilst one measure of air is passing in through the plaster. In a similar manner hydrogen would escape through minute openings with four times the velocity of oxygen; and laboratory experience shows that a cracked jar, or a bottle with a badly fitting stopper, may often be used to retain oxygen but not hydrogen.

A very striking illustration of the high rate of diffusion of hydrogen is arranged as represented in fig. 14. A is a cylinder of porous earthenware (such as are employed in galvanic batteries) closed at one end, and furnished at the other with a perforated caoutchouc stopper or a cork bung, through which passes a glass tube B, about six feet long, and half an inch in diameter. The bung is made air-tight by coating it with sealing wax dissolved in spirit of wine. This tube being supported so that its lower end dips about an inch below the surface of water, a jar of coal-gas is held over the porous cylinder, when the velocity of the particles of the gas is manifested by their being forced (not only out of the mouth of the jar C, which is open at the bottom, but also) through the pores of the earthenware jar, the air from which is violently driven out, as if by blowing, through the tube, and is seen bubbling up rapidly through the water. When the air has ceased to bubble out, and a large volume of gas has entered the porous jar, the bell-jar C is removed, when the gas escapes so rapidly through the pores, that a column of twenty to thirty inches of water is drawn rapidly up the tube B. If the greatest height to which the water ascends be marked, and when it has returned to its former level, a jar of hydrogen be held over the porous cylinder, it will be found that the above phenomena are manifested in a much higher degree, showing that coal-gas, being heavier than hydrogen, does not pass nearly so rapidly through the pores of the earthenware as hydrogen does.

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[*] Air being a mixture of nitrogen and oxygen, its rate of diffusion is intermediate between the rates of those gases; however, since the proportions of the gases are very nearly constant, no error of any magnitude arises.

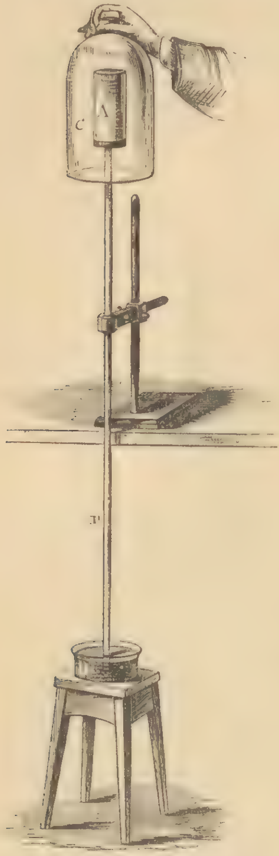

Fig. 14.

By connecting the porous cylinder A, by means of a short piece of tube, with a two-necked bottle, like that represented in fig. 10, and passing through a cork in the other neck, a piece of tube reaching to the bottom of the bottle and drawn out to an open point at its upper extremity (fig. 19), water may be forced out in a stream of two or three feet in height by holding the jar of hydrogen over the porous cylinder.

The great difference in the rates of diffusion of hydrogen and oxygen may be easily shown by the arrangement represented in fig. 15. A is a jar filled with a mixture of two volumes of oxygen with one volume of hydrogen, communicating through the stop-cock and flexible tube with the glass tube B, which is fitted through a perforated cork in the bowl of the common tobacco-pipe C, the sealing-waxed end of which dips under water in the trough D. By opening the stop-cock and pressing the jar down in the water, the mixed gases may be forced rapidly through the pipe, and if a small cylinder (E) be filled with them, the mixture will be found to detonate violently on the approach of a flame. But if the gas be made to pass very slowly through the pipe (at the rate of about a cubic inch per minute), the hydrogen will diffuse through the pores of the pipe so much faster than the oxygen, that the gas collected in the cylinder will contain so little hydrogen as to be no longer explosive, and to exhibit the property of oxygen to rekindle a partly extinguished match.

If two jars of the same size, one made of glass and the other of porous earthenware, be filled with the explosive mixture by holding them over the stop-cock of the jar A, and be then closed with glass plates and set aside for a few seconds, it will be found that the gas in the earthen jar will rekindle a spark on a match, whilst that in the glass jar will explode.

The rapid diffusion of hydrogen through paper may be shown by laying a flat piece of filter-paper upon the mouth of a cylinder of hydrogen, when the gas may be kindled on the upper surface. On repeating the experiment with a cylinder of coal-gas, only the pale flame of the hydrogen will appear above the paper. If a mixture of hydrogen and oxygen be employed, the hydrogen will be seen burning before the explosion takes place. A cylinder containing 2 vols. H and 1 vol. O, if covered with filter-paper, will be found to contain little else but oxygen after a minute or two.

14. *Chemical properties of hydrogen.*—The most conspicuous chemical property of hydrogen is its disposition to burn in air when raised to a moderately high temperature, entering into combination with the oxygen of the air to form water. The formation of water during the combustion of hydrogen gave rise to its name (ὕδωρ, water).

Since an *atom* of oxygen combines with two *atoms* of hydrogen to form water, the gases will not combine unless under the influence of some force, such as heat or electricity, to assist in resolving their *molecules* into the constituent atoms.

On introducing a taper into an inverted jar of hydrogen (fig. 16), the flame of the taper will be extinguished, but the hydrogen will burn with a pale flame at the mouth of the jar, and the taper may be rekindled at its flame by slowly withdrawing it.

The lightness and combustibility of hydrogen may be illustrated simultaneously by some interesting experiments. If two equal gas cylinders be filled with hydrogen, and held with their mouths respectively upwards and downwards, it will be found on testing each with a taper after the same interval, that the hydrogen has entirely escaped from the cylinder held with its mouth upwards, whilst the other still remains nearly filled with gas.

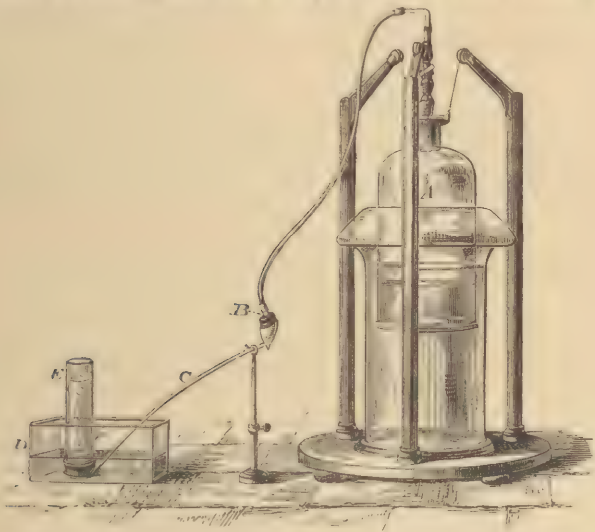

Fig. 15.—Separation of hydrogen and oxygen by atmolysis.*

The hydrogen may be scooped out of the jar A (fig. 17) with the small cylinder B attached to a handle. On removing B, and applying a taper to it, the gas will take fire.

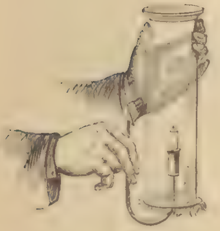
Fig. 16.

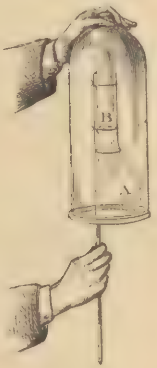

Fig. 17.

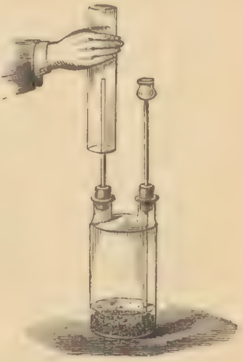
Fig. 18.

A cylinder may be filled with hydrogen by displacement of air (fig. 18), if the tube from the hydrogen bottle be passed up into it.

If such a dry cylinder of hydrogen be kindled whilst held with its mouth downwards, the formation of water during the combustion of the hydrogen will be indicated by the deposition of dew upon the sides of the cylinder.

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* This term has been applied to the separation of gases by diffusion; ἀτμός, *vapour*; λύω, to loosen.

By softening a piece of glass tube in the flame of a spirit-lamp, drawing it out and filing it across in the narrowest part (fig. 19), a jet can be made from which the hydrogen may be burnt. This jet may be fitted by a perforated cork to any common bottle for containing the zinc and sulphuric acid (fig. 20).

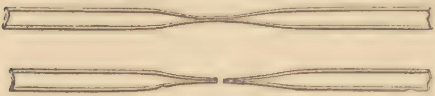

Fig. 19.

The hydrogen must be allowed to escape for some minutes before applying a light, because it forms an explosive mixture with the air contained in the bottle. This may be proved, without risk, by placing a little granulated zinc in a soda-water bottle, pouring upon it some diluted sulphuric acid, and quickly inserting a perforated cork, carrying a piece of glass tube about three inches long, and one-eighth of an inch wide. If this tube be immediately applied to a flame, the mixture of air and hydrogen will explode, and the cork and tube will be projected to a considerable distance.

By inverting a small test-tube over the jet in fig. 20, a specimen of the hydrogen may be collected, and may be kindled, to see if it burns quietly, before lighting the jet.

A dry glass, held over the flame, will collect a considerable quantity of water, formed by the combustion of the hydrogen.

The combustion of hydrogen produces a greater heating effect than that of an equal weight of any other combustible body. It has been determined that 1 grm. of hydrogen, in the act of combining with 8 grms. of oxygen, produces enough heat to raise 34462 grms. of water from 0° C. to 1° C. The temperature of the hydrogen flame is probably about 2024° C. Notwithstanding its high temperature, the flame of hydrogen is almost devoid of illuminating power, on account of the absence of solid particles.

15. If a taper be held several inches above a cylinder of hydrogen, standing with its mouth upwards, the gas will be kindled with a loud explosion, because an explosive mixture of hydrogen and air is formed in and around the mouth of the cylinder.

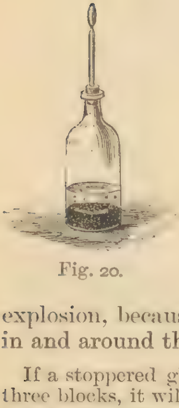

Fig. 20.

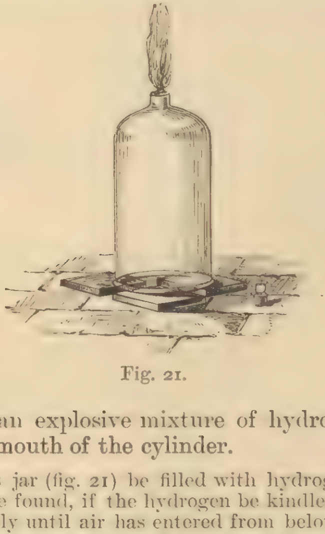

Fig. 21.

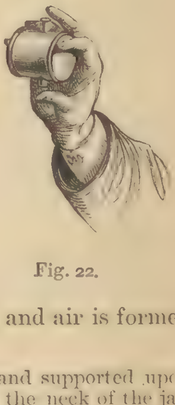

Fig. 22.

If a stoppered glass jar (fig. 21) be filled with hydrogen, and supported upon three blocks, it will be found, if the hydrogen be kindled at the neck of the jar, that it will burn quietly until air has entered from below in sufficient proportion to form an explosive mixture, which will then explode with a loud report.

The same experiment may be tried on a smaller scale, with the two-necked copper vessel (fig. 22), the lower aperture being opened some few seconds after the hydrogen has been kindled at the upper one.

The explosion of the mixture of hydrogen and air is due to the sudden expansion caused by the heat generated in the combination of the hydrogen with the oxygen throughout the mixture. After the explosion of the mixture of hydrogen and air (oxygen and nitrogen), the substances present are steam (resulting from the combination of the hydrogen and oxygen) and nitrogen, which are expanded by the heat developed in the combination, to a volume far greater than the vessel can contain, so that a portion of the gas and vapour issues very suddenly into the air around, the collision with which produces the report.

If pure oxygen be substituted for air, the explosion will be more violent, because the mixture is not diluted with the inactive nitrogen. The further study of this subject must be preceded by that of oxygen.

OXYGEN.

O = 16 parts by weight = 1 vol. 16 grains = 46.7 cub. in. at 60° F. and 30″ Bar.
16 grammes = 11.16 litres at 0° C. and 760 mm. Bar.

16. Oxygen is the most abundant of the elementary substances. It constitutes about one-fifth (by volume) of atmospheric air, where it is merely *mixed*, not combined, with the nitrogen, which composes the bulk of the remainder. Water contains eight-ninths (by weight) of oxygen; whilst silica and alumina, which compose the greater part of the solid earth (as far as we know it), contain about half their weight of oxygen.

Before inquiring which of these sources will most conveniently furnish pure oxygen, it will be desirable for the student to acquire some knowledge of the properties of this element, and of the chemical relations which it bears to other elementary bodies, for without such knowledge it will be found very difficult to understand the processes by which oxygen is procured.

17. *Physical properties of oxygen.*—From the fact of its occurring in an uncombined state in the atmosphere, it will be inferred that oxygen is perfectly invisible, and without odour. It is liquefied with difficulty, requiring a pressure of 320 atmospheres at − 140° C.* Oxygen gas is a little more than one-tenth heavier than air, which is expressed in the statement that its specific gravity is 1.1057.

In the study of theoretical chemistry, it is expedient to select hydrogen instead of air as the standard with which the specific gravities of gases are compared; for, since the atomic weights are also referred to hydrogen as the unit, and the atomic weights represent the weights of equal volumes, the numbers expressing the *atomic weights of the elementary gases are identical with their specific gravities* ($H = 1$). Thus the specific gravity of oxygen ($H = 1$) is 16. It will be found convenient to remember that *the specific gravity of a gas or vapour is the weight of one volume.*

Oxygen is slightly soluble in water; 100 volumes of water absorb 4 volumes of oxygen.

18. *Chemical properties of oxygen.*—This element is remarkable for the wide range of its chemical attraction for other elementary bodies, with all of which, except two, it is capable of entering into combination.

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* At this temperature, liquid oxygen has sp. gr. 0.88 (water = 1); it boils at − 184° C. under atmospheric pressure, and its absolute boiling point (critical temperature) is − 113° C.

Fluorine and bromine are the only elements which are not known to unite with oxygen.

With nearly all the elements oxygen combines in a direct manner; that is, without the intervention of any third substance.

There are only *seven elements* (among those of practical importance) *which do not unite in a direct manner with oxygen*, viz., *chlorine, bromine, iodine, fluorine, gold, silver, platinum.*

(Definition.—The compounds of oxygen with other elements are called *Oxides.*)

The act of combination with oxygen, or *oxidation*, is generally a slow process, and its effects are not immediately perceived. Some familiar examples of oxidation are—the tarnishing or rusting of metals by air, the gradual decay of wood, the *drying* of oils in paint, the formation of vinegar from alcoholic liquids, the respiration of animals, and combustion.

In all these processes heat is generated; but it is not usually noticed unless it is sufficient to render the particles of matter luminous, which is the case only with combustion.

(Definition.—*Combustion* is chemical combination attended with heat and light.)

Welter's law is approximately true for a large number of cases, that the quantity of heat produced by combustion is nearly proportional to the oxygen consumed, so that, for the same quantity of oxygen, different combustibles produce about the same quantity of heat. Thus, one gramme of oxygen produces about 4300 gramme units of heat with any combustible.

(The gramme unit of heat is the quantity of heat required to raise one gramme of water from 0° to 1° C.)

19. *Phosphorus, the only non-metal which combines with oxygen at the ordinary temperature*, affords a good illustration of oxidation. This element, a solid at the ordinary temperature, is preserved in bottles filled with water, on account of the readiness with which the oxygen of the air combines with it. If a small piece of phosphorus be dried by gentle pressure between blotting-paper, and exposed to the air, its particles begin to combine at once with oxygen, and the heat thus developed slightly raises the temperature of the mass.

Now, *heat generally encourages chemical union*, so that the effect of this rise of temperature is to induce a more extensive combination of the phosphorus with the oxygen, causing a greater development of heat in a given time, until the temperature is sufficient to render the particles brilliantly luminous, and a true case of combustion results—the combination of the phosphorus with oxygen, attended with production of heat and light. In cold weather, the phosphorus seldom takes fire until rubbed, or touched with a hot wire.

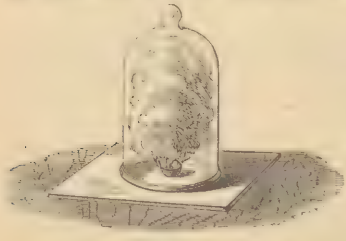

Fig. 23.

(Definition.—*Combustion in air* is the chemical combination of the elements of the combustible with the oxygen of the air, attended with development of heat and light.)

If a dry glass (fig. 23) be placed over the burning phosphorus, the thick white smoke which proceeds from it may be collected in the form of snowy flakes. These flakes are commonly termed *phosphoric oxide* or *anhydride*,* and are composed of 80 parts by weight of oxygen, and 62 parts of phosphorus (P_2O_5).

If the white flakes are exposed to the air for a short time, they attract moisture and become little drops, which have a very sour or *acid* taste. It was mentioned at page 14 that all substances which have such a taste have been found also to be capable of changing the blue colour of *litmus*† to red, whence the chemist is in the habit of employing paper dyed with blue litmus for the recognition of an acid.

(DEFINITION.—*Anhydride*, a compound which produces an acid when brought into contact with water.)

For the exact definition of an acid see page 29.

During the slow combination of phosphorus with the oxygen of the air, before actual combustion commences, only 48 parts of oxygen unite with 62 parts of phosphorus, forming the substance called *phosphorous oxide* or *anhydride* (P_2O_3).

(DEFINITION.—*The endings -ous and -ic* distinguish between two compounds formed by oxygen with the same element; *-ous* implying the smaller proportion of oxygen.)

Unless the temperature of the air be rather high, the fragment of phosphorus will not take fire spontaneously, but its combustion may always be ensured by exposing a larger surface to the action of the air. As a general rule, *a fine state of division favours chemical combination*, because the attractive force inducing combination operates only between substances in actual contact; and the smaller the size of the particles, the more completely will this condition be fulfilled.

Thus if a small fragment of dry phosphorus be placed in a test-tube, and dissolved in a little *carbon disulphide*, the solution when poured upon blotting paper (fig. 24), will part with the solvent by evaporation, leaving the phosphorus in a very finely divided state upon the surface of the paper, where it is so rapidly acted on by the oxygen of the air that it bursts spontaneously into a blaze.

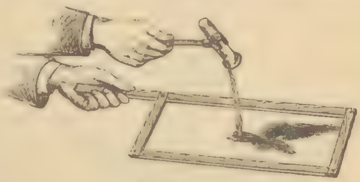
Fig. 24.

Though the light emitted by phosphorus burning in air is very brilliant, it is greatly increased when pure oxygen is employed; for since the nitrogen with which the oxygen in air is mixed takes no part in the act of combustion, it impedes and moderates the action of the oxygen. Each volume of the latter gas is mixed, in air, with four volumes of nitrogen, so that we may suppose five times as many particles of oxygen to come into contact, in a given time, with the particles of the phosphorus immersed in the pure gas, which will account for the great augmentation of the temperature and light of the burning mass.

To demonstrate the brilliant combustion of phosphorus in oxygen, a piece not larger than a good-sized pea is placed in a little copper or iron cup upon an iron stand (fig. 25), and kindled by being touched with a hot wire. The globe, having been previously filled with oxygen, and kept in a plate containing a little water, is placed over the burning phosphorus.*

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* *Anhydride*, or without water, from ἀν, negative, and ὕδωρ, water.

† A colouring matter prepared from a lichen, *Roccella tinctoria*; the cause of the change of colour will be more easily understood hereafter.

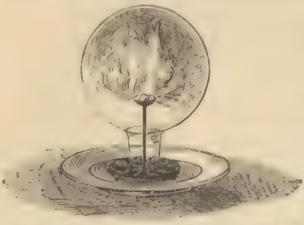

Fig. 25.—Phosphorus burning in oxygen.

It will be observed that the same white clouds of phosphoric anhydride are formed, whether phosphorus is burnt in oxygen or in air, exemplifying the fact that *a substance will combine with the same proportion of oxygen whether its combustion be effected in pure oxygen or in atmospheric air.* The apparent increase of heat is due to the combustion of a greater weight of phosphorus in a given time and space. The total heating effect produced by the combustion of a given weight of phosphorus is the same whether air or pure oxygen be employed.

20. Sulphur (*brimstone*) affords an example of a non-metallic element which will not enter into combination with oxygen until its temperature has been raised very considerably. When sulphur is heated in air, it soon melts; and as soon as its temperature reaches 500° F., it takes fire, burning with a pale blue flame. If the burning sulphur be plunged into a jar of oxygen, the blue light will become very brilliant, but the same act of combination takes place—32 parts by weight of oxygen uniting with 32 parts of sulphur to form *sulphurous acid gas* or *sulphurous anhydride* (SO_2), which may be recognised in the jar by the well-known suffocating smell of brimstone matches. The experiment is most conveniently performed by heating the sulphur in a *deflagrating spoon* (A, fig. 26), which is then plunged into the jar of oxygen, its collar (B) resting upon the neck of the jar, which stands in a plate containing a little water. The water absorbs a part of the sulphurous acid gas, and will be found capable of strongly reddening litmus-paper. It is possible to produce, though not by simple combustion, a compound of sulphur with half as much more oxygen (SO_3 sulphuric anhydride), showing that *a substance does not always take up its full share of oxygen when burnt.*

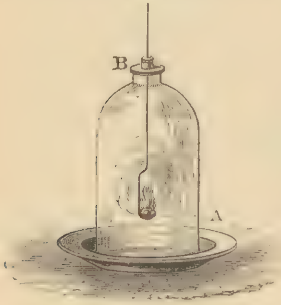

Fig. 26.—Sulphur burning in oxygen.

The luminosity of the flame of sulphur is far inferior to that of phosphorus, because, in the former case, there are no extremely dense particles in the flame corresponding to those of the phosphoric oxide produced in the combustion of phosphorus.

21. Carbon, also a non-metallic element, requires the application of a higher temperature than sulphur to induce it to enter into direct union with oxygen; indeed, perfectly pure carbon appears to require a heat approaching whiteness to produce this effect. But charcoal (the carbon in which is associated with not inconsiderable proportions of hydrogen and oxygen) begins to burn in air at a much lower temperature; and

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* This globe should be of thin, well-annealed glass: and it is sure to be broken if too large a piece of phosphorus be employed.

if a piece of wood charcoal, with a single spot heated to redness, be lowered into a jar of oxygen, the adjacent particles will soon be raised to the combining temperature, and the whole mass will grow intensely, 32 parts by weight of oxygen uniting with 12 parts of carbon to form *carbonic acid gas* (CO_2) or *carbonic anhydride*, which will redden a piece of moistened blue litmus-paper suspended in the jar. It should be remembered that *carbon is an essential constituent of all ordinary fuel, and carbonic acid gas is always produced by its combustion.*

It will be noticed that the combustion of the charcoal is scarcely attended with flame; and when pure carbon (diamond, for example) is employed, no flame whatever is produced in its combustion, because carbon is not convertible into vapour, and all *flame is vapour or gas in the act of combustion*; hence, *only those substances burn with flame which are capable of yielding combustible gases or vapours.*

22. The three examples of sulphur, phosphorus, and carbon sufficiently illustrate the tendency of non-metals to form acids by union with oxygen and water, which originally led to the adoption of its name, derived from ὀξύς, acid, and γεννάω, I produce. *All the non-metallic elements, except hydrogen and fluorine, are capable of forming anhydrides by their union with oxygen.*

Definition of an acid.—A compound containing hydrogen, which, when in contact with an alkali (p. 14) exchanges its hydrogen, or a portion of it, for the alkali metal.

For example—

HCl	+	$NaOH$	=	$NaCl$	+	H_2O
Hydrochloric acid.		Soda.		Sodium chloride.		Water.
H_2SO_4	+	$2KOH$	=	K_2SO_4	+	$2H_2O$
Sulphuric acid.		Potash.		Potassium sulphate.		Water.
H_3PO_4	+	$2NaOH$	=	Na_2HPO_4	+	$2H_2O$
Phosphoric acid.		Soda.		Sodium phosphate.		Water.

23. The metals, as a class, exhibit a greater disposition to unite directly with oxygen, though few of them will do so in their ordinary condition, and at the ordinary temperature. Several metals, such as iron and lead, are superficially oxidised when exposed to air under ordinary conditions, but this would not be the case unless the air contained water and carbonic acid gas, which favour the oxidation in a very decided manner. Among the metals which are of importance in practice, five only are oxidised by exposure to dry air at the ordinary temperature, viz., potassium, sodium, barium, strontium, and calcium, the attraction of these metals for oxygen being so powerful that they must be kept under petroleum, or some similar liquid free from oxygen. On the other hand, three of the common metals, silver, gold, and platinum, have so little attraction for oxygen that they cannot be induced to unite with it directly, even at high temperatures.

If a lump of sodium be cut across with a knife, the fresh surfaces will exhibit a splendid lustre, but will very speedily tarnish by combining with oxygen from the air, which gives rise to a coating of *sodium oxide*, and this to some extent protects the metal beneath from oxidation. The freshly cut sodium shines in the dark like phosphorus. Even when the attraction of the sodium for oxygen is increased by the application of heat, it is long before the mass of sodium is oxidised throughout, unless the temperature be sufficiently high to convert a portion of the sodium into vapour, which bursts through the crust of oxide, and burns with a yellow flame. If the spoon containing the sodium (see fig. 26) be now plunged into a jar of oxygen, the yellow flame will be far more brilliant.

Sixteen parts by weight of oxygen here combine with 46 parts of sodium to form disodium oxide (Na_2O), which remains in the spoon in a fused state. When the spoon is cool, it may be placed in water, which will dissolve the oxide, converting it into the alkali soda,

$$\underset{}{Na_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Soda.}}{2NaHO}$$

24. Zinc will serve as an example of a metal which has no disposition to enter into combination with oxygen at the ordinary temperature,* but which is induced to unite with it by a very moderate heat. If a little zinc (*spelter*) be melted in a ladle or crucible, and stirred about with an iron rod, it burns with a beautiful greenish flame, produced by the union of the vapour of zinc with the oxygen of the air. But the combustion is far more brilliant if a piece of zinc-foil be made into a tassel (fig. 27), gently warmed at the end, dipped into a little flowers of sulphur, kindled, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy. On withdrawing what remains of the tassel after the combustion is over, it will be found to consist of a brittle mass, which has a fine yellow colour while hot, and becomes white as it cools. This is the *zinc oxide* (ZnO), formed by the union of 16 parts by weight of oxygen with 65 parts of zinc.

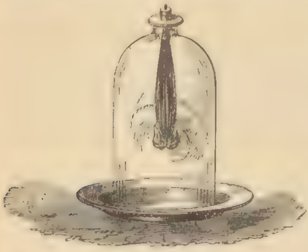
Fig. 27.—Zinc burning in oxygen.

The zinc oxide does not possess the properties of an acid or an alkali, and belongs to another class of compounds termed *bases*, which are not soluble in water as the alkalies are, but, like them, are capable of neutralising, either partly or entirely, the acids. Thus, if the zinc oxide were added to diluted sulphuric acid as long as the acid would dissolve it, the well-known corrosive properties of the acid would be destroyed, although it would still retain the power of reddening blue litmus, and the solution would now contain a new substance, or salt, called *zinc sulphate* ($ZnSO_4$).

(DEFINITION.—A *base* is a compound body which is capable of neutralising an acid, either partly or entirely.)

It will be observed that an *alkali* is only a particular species of base, and might be defined as *a base which is very soluble in water.*

(DEFINITION.—A *salt* is a compound formed when the hydrogen in an acid is replaced, either entirely or partly, by a metal; thus, sodium chloride, $NaCl$, is formed by the replacement of the H in HCl, hydrochloric acid, by sodium; sodium phosphate, Na_2HPO_4, is formed from phosphoric acid, H_3PO_4, by the replacement of two-thirds of the hydrogen by sodium.)

25. Iron, in its ordinary form, like zinc, is not oxidised by *dry* air or oxygen at the ordinary temperature; but if it be heated even to only 500° F. a film of oxide of iron forms upon its surface, and as the temperature is raised, the thickness of the film increases, until eventually it becomes so thick that it can be detached by hammering the surface, as may be seen in a smith's forge. If an iron rod as thick as the little

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* Unless water and carbonic acid gas be present, as in common air.

finger be heated to whiteness at the extremity, and held before the nozzle of a powerful bellows, it will burn brilliantly, throwing off sparks and dropping melted oxide of iron. If a stream of oxygen be substituted for air, the combustion is of the most brilliant description. A watch-spring (iron combined with about 1 per cent. of carbon) may be easily made to burn in oxygen by heating it in a flame till its elasticity is destroyed, and coiling it into a spiral (A, fig. 28), one end of which is fixed, by means of a cork, in the deflagrating collar B; if the other end be filed thin and clean, dipped into a little sulphur, kindled and immersed in a jar of oxygen (C) standing in a plate of water, the burning sulphur will raise the iron to the point of combustion, and the spring will be converted into molten drops of oxide.

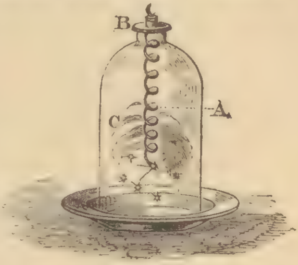

Fig. 28.—Watch-spring burning in oxygen.

The black oxide of iron formed in all these cases is really a combination of two distinct oxides of iron, one of which contains 16 parts by weight of oxygen and 56 parts of iron, and would be written FeO, whilst the other contains 48 parts of oxygen and 112 parts of iron, expressed by the formula Fe_2O_3. To distinguish them, the former is usually called *ferrous* oxide, and the latter *ferric* oxide; this combined with water constitutes ordinary rust.

The black oxide usually contains one combining weight of each oxide, so that it would be written $FeO.Fe_2O_3$, or Fe_3O_4. It is powerfully attracted by the magnet, and is often called magnetic oxide of iron. The abundant magnetic ore of iron, of which the *loadstone* is a variety, has a similar composition.

Iron in a very fine state of division will take fire spontaneously in air as certainly as phosphorus. *Pyrophoric* iron can be obtained (by a process to be described hereafter) as a black powder, which must be preserved in sealed tubes. When the tube is opened, and its contents thrown into the air, oxidation takes place, and is attended with a vivid glow. In this case the red oxide of iron is produced instead of the black oxide.

Both these oxides of iron are capable of neutralising, or partly neutralising, acids, and are, therefore, basic oxides or bases, like the oxides of zinc and sodium obtained in previous experiments. So general is the disposition of metals to form oxides of this class, that it may be regarded as one of the distinguishing features of a metal, for no non-metal ever forms a base with oxygen.

(DEFINITION.—A *metal* is an element capable of forming a base * by combining with oxygen.)

Many metals are capable also of forming anhydrides with oxygen; thus, tin forms stannic anhydride (SnO_2), antimony forms antimonic anhydride (Sb_2O_5), and it is always found that the anhydride of a metal contains a larger proportion of oxygen than any of the other oxides which the metal may happen to form.

26. There is a third class of oxides, termed the *indifferent oxides*,

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* The metal tungsten appears at present to be an exception to this rule, no well-defined basic oxide of this metal being known.

because they are neither anhydrides nor bases; such oxides may be formed either by non-metals or metals; thus water (H_2O), the oxide of hydrogen, is an indifferent oxide, and the black oxide of manganese (MnO_2) is an example of an indifferent metallic oxide.

27. *Preparation of oxygen.*—For almost all the useful arts in which uncombined oxygen is required, the diluted gas contained in atmospheric air is sufficient, since the nitrogen mixed with it does not interfere with its action.

From atmospheric air pure oxygen was first obtained by Lavoisier towards the end of the last century. His process is far too tedious to be employed as a general method of preparing oxygen, but it affords a very good example of the relation of heat to chemical action. Some mercury was poured into a glass flask with a long narrow neck, which was placed on a furnace, so that its temperature might be constantly maintained at about 349° C. (660° F.) for twelve days. The mercury boiled, and a portion of it was converted into vapour, which condensed in the neck of the flask and ran back again. Eventually part of the mercury was converted into a red powder, having combined with the oxygen of the air (or undergone *oxidation*) to form the *red oxide of mercury*. The nitrogen of the air does not enter into combination with the mercury.

By heating this oxide of mercury to a temperature approaching a red heat (about 500° C. or 1000° F.) it is decomposed into mercury and oxygen gas ($HgO = Hg + O$).

It is very generally found, as in this instance, that heat of moderate intensity will favour the operation of chemical attraction, whilst a more intense heat will annul it.

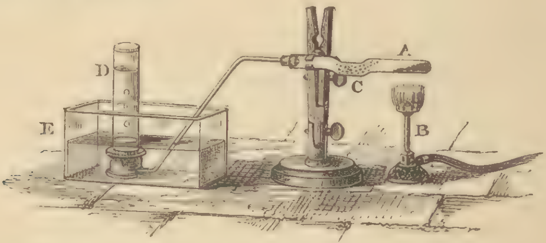

Fig. 29.—Preparation of oxygen from oxide of mercury.

For the purpose of experimental demonstration, the decomposition of the oxide of mercury may be conveniently effected in the apparatus represented by fig. 29, where the oxide is placed in the German glass tube A, and heated by the Bunsen's gas-burner B, the metallic mercury being condensed in the bend C, and the oxygen gas collected in the gas cylinder D, filled with water, and standing upon the bee-hive shelf of the *pneumatic trough* E. It may be identified by its property of kindling into flame the spark left at the end of a wooden match. If the heat be continued for a sufficient length of time, the whole of the oxide of mercury will disappear, being resolved into its elements. In technical language, the mercury is said to be *reduced*.

Upon the first application of heat the red oxide suffers a physical change, in consequence of which it becomes black; but its red colour returns again if it be allowed to cool.

A much cheaper process for obtaining unmixed oxygen from the air is now employed upon the large scale. It depends upon the principle that the oxides of manganese, when heated in contact with alkalies and air, are capable of absorbing the oxygen from the air, and of subsequently giving it up again if heated in a current of steam.

To illustrate this process, about four ounces of dry sodium manganate (which may be purchased cheaply in a crude state) are introduced into a porcelain tube* (*t*, fig. 30) fixed in a furnace. One end of the tube is connected with a two-branched glass tube, so that either a current of air may be passed through it by the tube *a*, or a current of steam from the flask *w*. On heating the manganate in the tube to dull redness, and passing the steam over it, oxygen is evolved, and may be collected in the jar *o*. $$\underset{\text{Sodium manganate.}}{2Na_2MnO_4} + 2H_2O = \underset{\text{Caustic soda.}}{4NaHO} + \underset{\text{Manganese sesquioxide.}}{Mn_2O_3} + O_3.$$

If the current of steam be discontinued and the air be slowly passed through the tube *a*, the oxygen of the air will be absorbed, and its nitrogen may be collected in the jar *n*. $$4NaHO + Mn_2O_3 + \underset{\text{Air.}}{3(O + N_4)} = 2Na_2MnO_4 + 2H_2O + N_{12}.$$

If the proper temperature be employed, the stream of gas issuing from the tube may be constantly kept up, and may be made to consist of oxygen or nitrogen accordingly as steam or air is passed through the tube. The current of air is regulated by the nipper-tap *c*.

The gas-furnace represented in fig. 30 consists of a row of twelve Bunsen burners, each having a stop-cock by which the flame is regulated. The horizontal pipe *b*, from which they spring, is capable of being raised or lowered at pleasure. The porcelain tube *t* is laid in a semi-cylindrical trough made of stout iron rods, and filled with pieces of pumice-stone or fire-brick. Above this is placed a corresponding trough, so that the tube is entirely surrounded by glowing material.† The heat must be applied gradually to avoid splitting the tube.

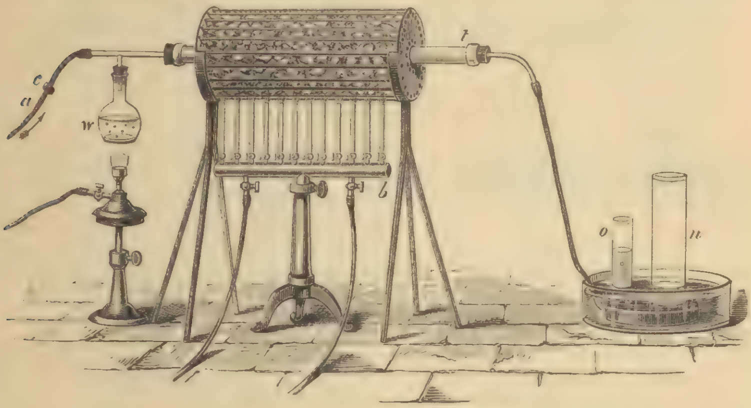

Fig. 30.—Extraction of oxygen from air.

28. The only other natural source from which it has been found convenient to prepare pure oxygen, is a black mineral composed of manganese and oxygen. It is found in some parts of England, but much more abundantly in Germany and Spain, whence it is imported for the use of the bleacher and glass-maker. Its commercial name is *manganese*, but it is known to chemists as *binoxide of manganese* or

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* A copper tube with screw-caps, into which narrow brass or copper tubes are brazed, may be advantageously substituted for the porcelain tube. The process is much facilitated by mixing the manganate of soda with an equal weight of oxide of copper.

† This burner, as well as the burner described at page 13, was constructed for me by Mr. Rowley, formerly of the Royal Military Academy, Woolwich, whose readiness in perceiving the intention of an apparatus, and in improving upon the original idea as the work proceeded, rendered his co-operation in arranging experimental illustrations of the greatest service to me.

manganese dioxide (MnO_2), and to mineralogists by several names designating different varieties. The most significant of these names is *pyrolusite*, referring to the facility with which it may be decomposed by heat (πῦρ, fire, and λύω, to loosen).

One of the cheapest methods of preparing oxygen consists in heating small fragments of this black oxide of manganese in an iron retort, placed in a good fire, the gas being collected in jars filled with water, and standing upon the shelf of the pneumatic trough, or in a gas-holder or gas-bag, if large quantities are required.

The attraction existing between manganese and oxygen is too powerful to allow the metal to part with the whole of its oxygen when heated, so that only one-third of the oxygen is given off in the form of gas, a brown oxide of manganese being left in the retort; $3MnO_2 = Mn_3O_4 + O_2$.

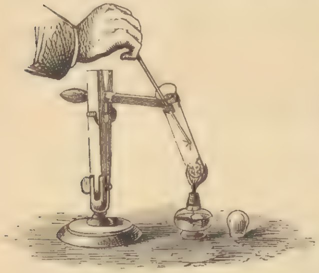

Fig. 31.

29. By far the most convenient source of oxygen, for general use in the laboratory, is the artificial salt called *chlorate of potash*, or *potassium chlorate*, which is largely manufactured for fireworks, percussion-cap composition, &c. If a few crystals of this salt be heated in a test-tube over a spirit-lamp (fig. 31), it soon melts to a clear liquid, which presently begins to boil from the disengagement of bubbles of oxygen, easily recognised by introducing a match with a spark at the end into the upper part of the tube. If the action of heat be continued until no more oxygen is given off, the residue in the tube will be the salt termed potassium chloride;

$$\underset{\text{Potassium chlorate.}}{KClO_3} = \underset{\text{Potassium chloride.}}{KCl} + O_3.$$

To ascertain what quantity of oxygen would be furnished by a given weight of the chlorate, the atomic weights must be brought into use. Referring to the table of atomic weights, it is found that $K = 39$, $O = 16$, and $Cl = 35.5$; hence the molecular weight of potassium chlorate is easily calculated.

One atomic weight of potassium	39
,, ,, chlorine	35.5
Three atomic weights of oxygen	48
	$KClO_3 = 122.5$

So that 122.5 grains of chlorate would yield 48 grains of oxygen.

Since 16 grains of oxygen measure 46.7 cubic inches (p. 25), the 48 grs. will measure 140 cubic inches.

Hence it is found that 122.5 grains of potassium chlorate would give 140 cubic inches of oxygen measured at 60° F. and 30 in. Bar.

If one gallon (277.276 cubic inches) of oxygen be required, 242.6 grains of chlorate must be used, or rather more than half an ounce.

122.5 grammes of potassium chlorate would yield 33.48 litres of oxygen measured at 0° C. and 760 mm. Bar.

Since the complete decomposition of the potassium chlorate requires a more intense heat than a glass vessel will usually endure, it is customary to facilitate it by mixing the chlorate with about one-fifth of its weight of powdered black oxide of manganese, when the whole of the oxygen is given off at a comparatively low temperature, though the oxide of manganese itself suffers no change, and its action has not yet received any explanation which is quite satisfactory.

Fig. 32 shows a very convenient arrangement for preparing and collecting oxygen for the purpose of demonstrating its relations to combustion. A is a Florence flask in which the glass tube B is fixed by a perforated cork. C is a tube of vulcanised india-rubber. The gas-jar is filled with water, and supported upon a bee-hive shelf made of earthenware. If pint gas-jars be employed, 300 grains of potassium chlorate, mixed with 60 grains of binoxide of manganese, will furnish a sufficient supply of gas for the ordinary experiments. The binoxide of manganese should be thoroughly dried by moderately heating it in a crucible before being mixed with the chlorate. It is also advisable to test it by heating a little of it with the chlorate, since charcoal and sulphuret of antimony, which form very explosive mixtures with chlorate of potash, have sometimes been sold by mistake for binoxide of manganese. The heat must be moderated according to the rate at which the gas is evolved, and the tube C must be taken out of the water before the lamp is removed, or the contraction of the gas in cooling will suck the water back into the flask. The first jar of gas will contain the air with which the flask was filled at the commencement of the experiment. The oxygen obtained will have a slight smell of chlorine.

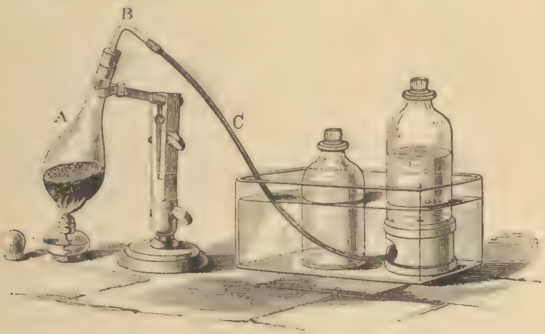

Fig. 32.—Preparation of oxygen.

WATER.

$H_2O = 18$ grammes $= 22.32$ litres (vapour).

30. *Synthesis of Water from its Elements.*—It has been seen already (p. 24) that the combination of hydrogen with oxygen to form water is attended with great evolution of heat and consequent expansion, and hence the mixture of these gases is found to explode violently on contact with flame.

The experiment may be made safely in a soda-water bottle. The bottle is filled with water, and inverted with its mouth beneath the surface of the water; enough oxygen is then passed up into it to fill one-third of its volume; if the remainder of the water be then displaced by hydrogen, and the mouth of the bottle be presented to the flame of a spirit-lamp, a very violent explosion will result, attended with a vivid blue flash in the bottle. If the mouth of the bottle be presented towards a screen of paper, at a distance of 20 or 30 inches, the paper will be violently torn to pieces, bearing witness to the concussion between the expanded steam issuing from the bottle and the external air.

If some of the mixture of oxygen with twice its volume of hydrogen be introduced into a capped jar (fig. 33), provided with a piece of caoutchouc tubing and a small glass tube, and pressed down in a trough of water, soap-bubbles may be inflated with it, which will ascend rapidly in the air, and explode violently when touched with a flame, which must not, of course, be applied to the bubble until it is at some distance away from the tube, for fear of exploding the mixture in the jar.

31. In order to demonstrate the production of water in the explosion, the

Cavendish eudiometer * (fig. 34) is employed. This is a strong glass vessel, with a stopper firmly secured by a clamp (A), and provided with two platinum wires (P), which pass through the stopper, and approach very near to each other within the eudiometer, so that the electric spark may easily be passed between them. By screwing the stop-cock B into the plate of an air-pump, the eudiometer may be exhausted. It is then screwed on to the jar represented in fig. 35, which contains a mixture of two measures of hydrogen with one measure of oxygen, standing over water. On opening the stop-cocks between the two vessels, the eudiometer becomes filled with the mixture, and the quantity which has entered is indicated by the rise of the water in the jar. The glass stop-cock C having been closed to prevent the brass cap from being forced off by the explosion, the eudiometer is again screwed on to its foot, and an electric spark passed between the platinum wires, either from a Leyden jar or an induction-coil, when the two gases will combine with a vivid flash of light,† attended with a very slight concussion, since there is no collision with the external air. For an instant a mist is perceived within the eudiometer, which condenses into fine drops of dew, consisting of the water formed by the combination of the gases, which was here induced by the

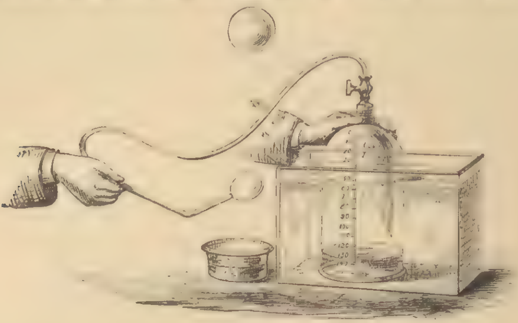

Fig. 33.

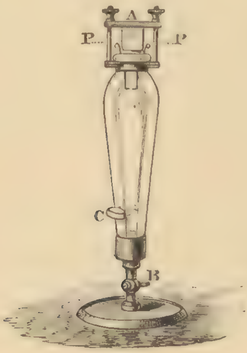

Fig. 34.

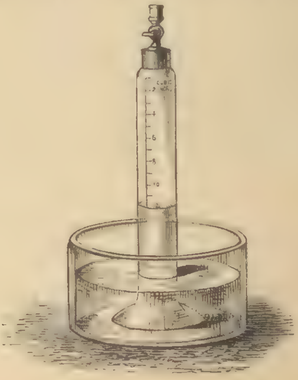

Fig. 35.

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* So named from εὔδιος, fine or clear, and μέτρον, a measure, because an instrument upon the same principle has been used to determine the degree of purity of the atmosphere. The eudiometer was employed by Cavendish about the year 1770, for the synthesis of water.

† Since the steam produced at the moment of combination is here prevented from expanding, the heat which would have expanded it is saved, so that the temperature is higher and the flash of light brighter than when the combination is effected in an open vessel.

high temperature of the electric spark, as it was in the former experiment by the high temperature of the flame. If the gases have been mixed in the exact proportion of two measures of hydrogen to one measure of oxygen, the eudiometer will now be again vacuous, and if it be screwed on to the capped jar, may be filled a second time with the mixture, which may be exploded in the same manner.

The entire disappearance of the gases may be rendered obvious to the eye by exploding the mixture over mercury. For this purpose the mixed gases should be collected from water itself, which is strongly acidified with sulphuric acid, and decomposed in the *voltameter* (A, fig. 36) by the aid of five or six cells of Grove's battery. The voltameter contains two platinum plates (B), attached to the platinum wires C and D, which are connected with the opposite poles of the battery. The first few bubbles of the mixture of hydrogen and oxygen evolved having been allowed to escape, in order to displace the air, the gas may be collected in the small eudiometer (E), which has been previously filled with water. This eudiometer is a cylinder of very thick glass,* closed at one end, and having two stout platinum wires cemented into holes drilled near the closed end, the wires approaching sufficiently near to each other to allow the passage of the electric spark. Having been filled with the mixture of hydrogen and oxygen from the voltameter, the eudiometer is closed with the finger, and transferred to a basin containing mercury, where it is pressed firmly down upon a stout cushion of india-rubber, and the spark passed through the mixed gases, either from the coil or the Leyden jar. The combustion takes place with violent concussion, but without noise; and since the eudiometer is vacuous after the gases have combined, the cushion will be found to be very firmly pressed against its open end. On loosening the cushion, the mercury will be violently forced up into the eudiometer, which will be completely filled with it, proving that when an electric spark is passed through the mixture of 2 volumes of hydrogen and 1 volume of oxygen, no residue of gas remains.

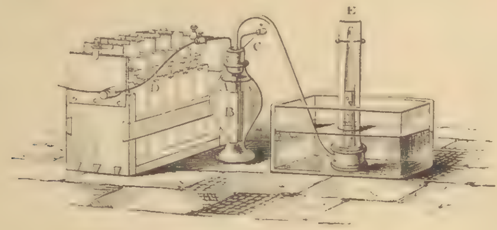

Fig. 36.—Detonating gas collected from voltameter.

This may also be demonstrated with the siphon eudiometer, shown in fig. 37, by confining about a cubic inch of the explosive mixture in the closed limb, over water, and stopping the open limb securely with a cork, so as to leave a space filled with air between the cork and the water. The eudiometer must be very firmly fixed on a stand, or it will be broken by the concussion. After it has been proved, it may be held in the hand, as in the figure. By firing mixtures of hydrogen and oxygen, in different proportions, in the same manner, it may be shown that any excess of either gas above the ratio of 2H : O will remain uncombined after the explosion. Care is required in these experiments, since eudiometers are often burst by the explosion of the mixture of 2 volumes of hydrogen with 1 volume of oxygen.

The explosion and the flash of light in the foregoing experiments are both the results of the heat generated in the act of combination; so that the water produced represents so much less *energy* as corresponds to the heat given off in the combination. This heat has been measured by means of a *calorimeter*, and it has been found that 2 grammes of H and 16 grms. of O, in combining to form liquid water, generate enough heat to raise 68924 grms. of water from 0° C. to 1° C. Of this quantity, 9666 represent the heat generated by the change of state from the gas to the liquid, so that the difference, 59258, represents the heat generated by the chemical action occurring between hydrogen and oxygen in forming a molecule of water in the state of gas. This may be expressed by $H_2 + O = H_2O +$ 59258 *heat-units*, the heat-unit being the quantity of heat required to raise the temperature of one gramme of water from 0° C. to 1° C.

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* The bore of the eudiometer should be about half an inch in diameter, and the thickness of its sides about ⅜ths of an inch; its length is 7 inches.

The quantity of heat produced in any chemical action is a measure of the amount of chemical force which is exerted. To decompose 18 grammes of steam we must employ an amount of force, in the form, for example, of electricity, corresponding to 59258 heat-units.

32. The knowledge of the volumes in which hydrogen and oxygen combine, is turned to account in the analysis of gases, to ascertain the proportion of hydrogen or oxygen contained in them. Suppose, for example, it be required to determine the amount of oxygen in a sample of atmospheric air; the latter is mixed with hydrogen, in more than sufficient quantity to combine with the largest proportion of oxygen which could be present, and when the combination has been induced by the electric spark, the volume of gas which has disappeared (2 volumes H + 1 volume O) has only to be divided by three to give the volume of the oxygen.

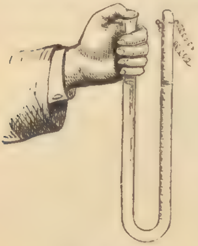

Fig. 37.
Siphon eudiometer.

A bent eudiometer (fig. 37) is generally employed for this purpose. Having been completely filled with water, it is inverted in the trough, and the specimen of air is introduced (say 0.5 cubic inch or 8 cubic centimetres). The open limb is then closed by the thumb, and the eudiometer turned so as to transfer the air to the closed limb. A stout glass rod is thrust down the open limb, so as to displace enough water to equalise the level in both limbs, in order that the volume of the air may not be diminished by the pressure of a higher column of water in the open limb. The volume of the included air having been accurately noted, the open limb of the tube is again filled up with water, inverted in the trough, and a quantity of hydrogen introduced, equal to about half the volume of the air. This having been transferred, as before, to the closed limb, the columns of water are again equalised, and the volume of the mixture of air and hydrogen ascertained. The open limb is now firmly closed with the thumb, and the electric spark passed through the mixture, either from the Leyden jar or the induction-coil. On removing the thumb, after the explosion, the volume of gas in the closed limb will be found to have diminished very considerably. Enough water is poured into the open limb to equalise the level, and the volume of gas is observed. If this volume be subtracted from the volume before explosion, the volume of gas which has disappeared will be ascertained, and one-third of this will represent the oxygen, which has condensed with twice its volume of hydrogen into the form of water. Thus the numbers recorded will be—

Volume of air analysed	0.50	cub. in.
Volume of air mixed with hydrogen . . .	0.75	,,
After explosion	0.45	,,
Difference (⅔H and ⅓O)	.30	,,

.30 divided by three = .10 cub. in. of oxygen.

In exact experiments, a correction would be required for any variation of the temperature or barometric pressure during the progress of the analysis.

33. It will have been observed, in the experiment upon the synthesis of water in the Cavendish eudiometer, that the volume of water obtained is very small in comparison with that of the gases before combination,

about 1870 volumes of the mixed gases being required to form one volume of liquid water, because, after the *chemical* attraction has caused the molecules of H and O to form steam, the *cohesive* attraction has caused the molecules of steam to unite and form liquid water. In order to watch the effect of the chemical attraction only, we must prevent the steam from changing its state after it is produced.

If the mixture of hydrogen and oxygen be measured and exploded at or above the boiling point of water, it is found that the steam produced occupies two-thirds of the volume of the mixed gases, measured at the same temperature and atmospheric pressure. Hence, *two volumes of hydrogen combine with one volume of oxygen to form two volumes of aqueous vapour, at the same temperature and pressure.*

The combination of hydrogen and oxygen in a vessel heated to the boiling point of water is effected in the apparatus contrived by Dr. Hofmann, and represented in fig. 38, where the closed limb of the eudiometer is surrounded by a tube through which steam is passed from a flask connected with the wide tube by a cork and a short wide piece of bent glass tubing, jacketed with caoutchouc to prevent loss of heat. The steam escapes through the tube *t* which enters the cork at the bottom. The closed limb of the eudiometer having been filled with mercury, a small quantity of the mixture of hydrogen and oxygen obtained from the voltameter (fig. 36) is introduced into it through a tube passed down the open limb, the displaced mercury being run out through the tube *c*, which is closed by a nipper-tap. The closed limb is then heated by the steam, and the mercury in the two limbs levelled from time to time by running a little out through *c*, until the gas in the closed limb no longer expands. Its volume is then observed, an inch more mercury poured into the open limb, which is then tightly closed by a cork, and the spark from the induction-coil (fig. 6) is passed by the wires − and +. After the explosion, the cork is removed, and the mercury levelled in the two limbs, when the volume of the steam will be found to be just two-thirds of the volume of the gas before the explosion. On cooling down, the steam condenses, and the mercury entirely fills the closed limb of the eudiometer.

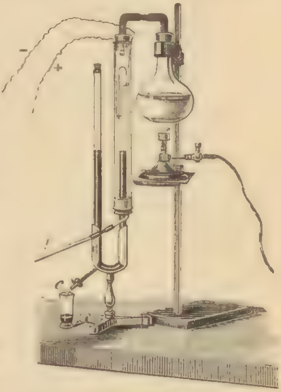

Fig. 38.—Synthesis of water at 100° C.

That 2 volumes of steam should contain 2 volumes of hydrogen and 1 volume of oxygen would appear, on physical grounds, impossible, since two bodies cannot occupy the same space at the same time; but it must be remembered that the two bodies in question have lost their individuality in consequence of their chemical combination, by which they have become one body—water.

34. The synthesis of water by weight cannot be effected with accuracy by weighing the gases themselves, on account of their large volume. It is therefore accomplished by passing an indefinite quantity of hydrogen over a known weight of pure hot oxide of copper, when the hydrogen combines with the oxygen of the oxide to form water. The loss of weight suffered by the oxide of copper gives the amount of oxygen; and if this be deducted from the weight of the water, that of the hydrogen will be ascertained.

The apparatus employed for this purpose is represented in fig. 39. *h* is the bottle in which hydrogen is generated from diluted sulphuric acid and zinc; the gas passes in *p* through solution of potash, which absorbs any sulphuretted hydrogen; then through *s*, containing pumice-stone (used on account of its porous character), saturated with a strong solution of silver nitrate, which removes arsenic and antimony from the hydrogen; the gas then passes through *vv*,

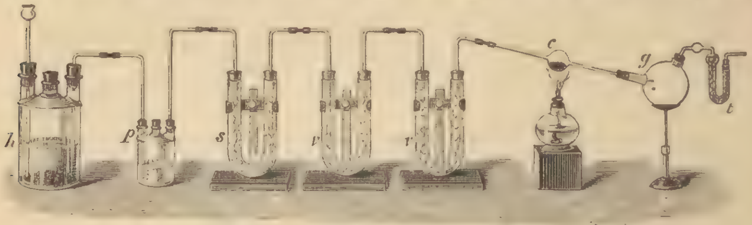

Fig. 39.—Synthesis of water by weight.

containing pumice saturated with oil of vitriol to absorb moisture. The bulb *c*, with the oxide of copper, is weighed before and after the experiment, as are the globe *g*, for condensing the water, and the tube *t*, containing pumice and oil of vitriol, to absorb the aqueous vapour. Of course the bulb *c* must not be heated until the hydrogen has displaced all the air from the apparatus.

As an example, 10 grammes of CuO were employed, and 7.98 grms. Cu were left, 2.2725 grms. water being collected. $10-7.98=2.02$ grms. O; $2.2725-2.02=.2525$ grms. H; $2.2725 : 2.02 :: 100 : 88.88$; $2.2725 : .2525 :: 100 : 11.11$. 100 parts by weight of water, therefore, contain 88.88 O and 11.11 H. This is the usual method of stating the composition of a substance. To deduce the chemical formula, we must divide each constituent by its atomic weight; $88.88 \div 16 = 5.5$ atomic weights of O; $11.11 \div 1 = 11.11$ atomic weights of H. Then $5.55 : 11.11 :: 1$ atom O : 2 atoms H.

The formula would be $H_2O = 18$ weights, and since 18 grammes of water converted into steam are found to occupy the same volume as 2 grammes (or one molecular weight) of hydrogen, H_2O represents one molecule of water.

The above experiment would also serve for fixing the atomic weight of copper, for it shows that 100 parts by weight of cupric oxide contain 79.8 parts of copper and 20.2 parts of oxygen. Then $20.2 : 79.8 :: 16 : 63.2$; so that if cupric oxide contains one atom of copper to one atom of oxygen, the atomic weight of copper would be 63.2.

There is another oxide of copper known, which contains 127 of copper to 16 of oxygen, and if 63.5 be taken as the atomic weight of copper, we shall have

Black oxide	CuO	$63.5\ Cu : 16\ O$
Red ,,	Cu_2O	$127\ Cu : 16\ O$

and this would account for the disposition of the red oxide to decompose into CuO and metallic Cu, as well as for some of its other properties.

35. It is evident that, although hydrogen is generally designated the combustible gas, and oxygen the supporter of combustion, the application of these terms depends entirely upon circumstances, since the phenomenon of combustion is a reciprocal operation in which both elements have an equal share.

This may be illustrated by a simple experiment. The hydrogen and oxygen reservoirs,* H and O, fig. 40, are connected with two bent glass tubes passing through a cork into an ordinary lamp glass *c*, upon the upper opening of which a plate of talc is laid. In order to prevent the ends of the glass tubes from being fused by the burning gases, little platinum tubes, made by rolling up pieces of platinum foil, are placed in the orifices, and the glass is melted round them by the blowpipe flame. The hydrogen being lighted, and the oxygen turned on to about the same extent, the lamp-glass is placed over the cork, when the hydrogen burns steadily. If the oxygen be slowly turned off, the flame will gradually leave the hydrogen tube and come over to the oxygen, which will continue burning in the atmosphere of hydrogen. By again turning on the oxygen, the flame may be sent over to the hydrogen tube. With a little care the flame may be made to occupy an intermediate position between the two burners, and to leap from one to the other at pleasure.

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* These are the wrought-iron vessels in which hydrogen and oxygen are condensed under the pressure of a few atmospheres by Mr. Orchard of Kensington. They are far more convenient than gas-bags or gas-holders.

36. The great energy with which hydrogen combines with oxygen is turned to account for the purpose of producing the highest temperature which can be obtained by any chemical process.

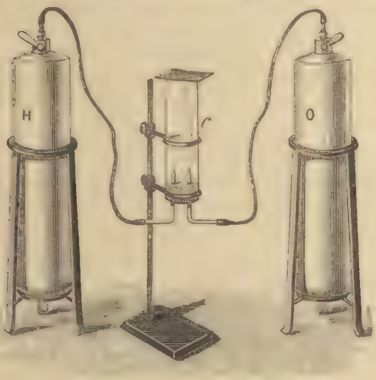

Fig. 40.—Reciprocal combustion.

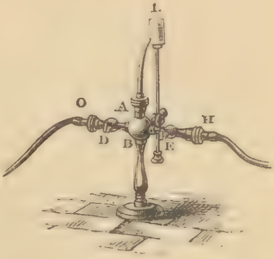

Fig. 41.—Oxyhydrogen blowpipe.

The *oxyhydrogen* blowpipe (fig. 41) is an apparatus for burning a jet of hydrogen mixed with half its volume of oxygen. The gases are supplied from separate gas-holders (or bags with pressure-boards and weights) through the tubes H and O, which conduct them into the brass sphere B. Each of these tubes is provided with a valve of oiled silk opening outwards, so as to prevent the passage of either gas into the receptacle containing the other. The tube A is stuffed with thin copper wires, which would rapidly conduct away the heat and extinguish the flame of the mixed gases burning at the jet, should it tend to pass back and ignite the mixture in B. The stop-cocks D and E allow the flow of the gases to be regulated so that they may mix in the right proportions. If the hydrogen be kindled first, it will be found that, as soon as the oxygen is turned on, the flame is reduced to a very much smaller volume, because the undiluted oxygen required to maintain it occupies only one-fifth of the volume of the atmospheric air, from which the hydrogen was at first supplied with oxygen. The heat developed by the combustion being therefore distributed over a much smaller area, the temperature at any given point of the flame must be much higher, and very few substances are capable of enduring it without fusion.* Lime is one of these; and if a cylinder of lime be supported, as at L (fig. 41), in the focus of the flame, its particles become heated to incandescence, and a light is obtained which is visible at night from very great distances, so as to be well adapted for signalling and light-houses. For such purposes coal-gas is often used instead of hydrogen (*oxycalcium* light).

If a shallow cavity be scooped in a lump of quicklime, a few scraps of platinum placed in it, and exposed to the oxyhydrogen flame (fig. 42), a fused globule of platinum of very considerable size may be obtained in a few seconds. By employing a little furnace made of lime, Deville has succeeded in fusing platinum in quantities sufficient to cast large ingots, a result unattainable by any other furnace. Pipeclay, which resists the action of all ordinary furnace-heats, may be fused into a glass

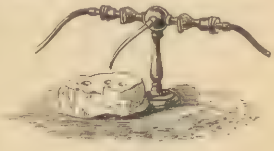

Fig. 42.

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* The temperature of the hydrogen flame in air is about 2000° C., while in oxygen it is over 2800°. The last temperature could not be surpassed, because it is that at which steam is *dissociated* or resolved into its elements, which re-combine as soon as the temperature falls below that point.

in this flame, whilst gold and silver are instantaneously melted, and vaporised into a dense smoke.

37. In its chemical relations to other elements, hydrogen is diametrically opposed to oxygen. Whereas the latter combines directly with the greater number of the elements, hydrogen will enter into direct combination with very few; all the metals form compounds with oxygen, but very few combinations of metals with hydrogen have been obtained. Indeed, in its relations to other elements, hydrogen closely resembles the metals, though it does not fall within the definition of a metal given above, since it does not form a base with oxygen, and its combinations with the salt-radicals (chlorine, &c.) are acids, and not salts, as is the case with metals.

38. *Chemical Relations of Water to other Substances.*—In its chemical relations water presents this very remarkable feature, that, although it is an *indifferent oxide*, its combining tendencies extend over a wider range than those of any other compound. Its combinations with other substances are generally called *hydrates*. Water combines with two of the elementary substances, viz., chlorine and bromine, but no other element is even dissolved by water in any considerable quantity. One part of iodine is dissolved by 500 parts of cold water, but no chemical combination appears to take place. Oxygen, hydrogen, and nitrogen are dissolved by water in very small quantity, but become only mechanically diffused through it, and do not enter into chemical combination.

When water acts upon a compound body, it may either effect a *simple solution*, or may enter into chemical combination with it.

Simple solution appears to be a purely physical phenomenon not accompanied, of necessity, by any chemical action. The dissolved substance, in such cases, is otherwise unchanged in properties, and there is no manifestation of heat, as in cases of chemical combination. On the contrary, there is a reduction of temperature, such as is always noticed in the merely physical change from the solid to the liquid form. For example, common saltpetre (nitre or nitrate of potash), when shaken with water, is rapidly dissolved, the water becoming sensibly colder. If fresh portions of saltpetre be added till the water is unable to dissolve any more, it will be found that 1000 grs. of water (at 60° F.) have dissolved about 300 grs. of saltpetre. Such a solution would be called a *cold saturated solution* of saltpetre. If the solution be set aside in an open vessel, the water will slowly pass off in vapour, and the saltpetre will be gradually deposited, its particles arranging themselves in the regular geometrical shape of the six-sided prism, which is its common *crystalline form*. The crystals of saltpetre do not contain any water: they are *anhydrous*.

If saltpetre be added to boiling water (in a porcelain evaporating dish, fig. 43), and stirred (with a glass rod) until the water refuses to dissolve any more, 1000 grs. of water will be found to have dissolved about 2000 grs.; this would be called a *hot saturated solution*.

As a general rule, solids are dissolved more quickly and in larger quantity by hot water than by cold.

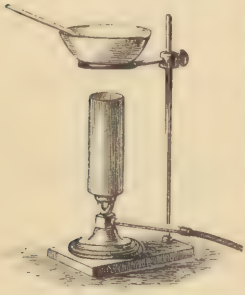

Fig. 43.

One of the commonest methods of *crystallising* a solid substance consists in dissolving it in hot water and allowing the solution to cool slowly. The more slowly it cools, the larger and more symmetrical are the crystals.

A hot saturated solution is not generally the best for crystallising, because it deposits the dissolved body too rapidly. Thus the hot solution of saltpetre prepared as above would solidify to a mass of minute crystals on cooling; but if 1000 grs. of saltpetre be dissolved in 4 measured ounces of boiling water, it will form crystals of 2 or 3 inches long when slowly cooled (in a covered vessel). If the solution be stirred while cooling, the crystals will be very minute, having the appearance of a white powder.

Some solids, however, refuse to crystallise, even from a hot saturated solution, if it be kept absolutely undisturbed.

Sodium sulphate affords a good example of this. If the crystallised sulphate be added to boiling water in a flask, as long as it is dissolved, the water will take into solution more than twice its weight of the salt, yielding a solution which boils at 220° F. If this solution be allowed to cool in the open flask, an abundant crystallisation will take place, for cold water will dissolve only about one-third of its weight of crystallised sulphate. But if the flask (which should be globular) be tightly corked whilst the solution is boiling, it may be kept for several days without crystallising, although moved about from one place to another. In this condition the solution is said to be *super-saturated*. On withdrawing the cork, the air entering the partly vacuous space above the liquid will be seen to disturb the surface slightly, and from that point beautiful prismatic crystals will shoot through the liquid until the whole has become a nearly solid mass. A considerable elevation of temperature is observed, consequent upon the passage from the liquid to the solid form. If the solution of sodium sulphate be somewhat weaker, containing exactly two-thirds of its weight of the crystals, it may be cooled without crystallising, even in vessels covered with glass plates, but a touch with a glass rod will start the crystallisation immediately.

The crystallisation of a super-saturated solution is provoked by contact with a crystal of the salt itself. Minute crystals of sodium sulphate are present in the floating dust of the air, and cause the crystallisation when they fall into the super-saturated solution. A perfectly clean glass rod may be dipped into the liquid without causing crystallisation, but a rod which has been exposed to air will have some particles of sodium sulphate on it, and will start crystallisation; if the rod be heated so as to render the sodium sulphate from the dust anhydrous, it will no longer cause crystallisation unless it be drawn through the hand. Air filtered through cotton wool does not cause super-saturated solutions to crystallise. If the solution of sodium sulphate containing two-thirds of its weight of the crystals be allowed to cool in a flask closed by a cork furnished with two tubes plugged with cotton wool, it will be found that, on withdrawing the plugs and blowing through one of the tubes dipping into the solution, crystallisation does not take place, but if air be blown by a pair of bellows into the same solution it will crystallise at once.

Sodium hyposulphite (thiosulphate) and sodium acetate yield super-saturated solutions which are less likely to be crystallised by dust than the sodium sulphate. If a warm super-saturated solution of sodium acetate be very carefully poured upon a cold super-saturated solution of sodium hyposulphite, in a narrow cylinder, which is then covered and allowed to cool, a crystal of the hyposulphite may be dropped in without causing crystallisation till it reaches the lower layer of hyposulphite solution; a crystal of sodium acetate may then be dropped in to start the crystallisation of the upper layer.

Super-saturated solution of sodium acetate is used in railway foot-warmers, where the heat evolved in the crystallisation renders it four times as efficacious as the same volume of hot water.

A most beautiful illustration of the power of unfiltered air to start crystallisation is afforded by a solution of alum which has been saturated at 194° F. (90° C.)*

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* J. M. Thomson recommends a solution of alum in half its weight of water for this experiment.

and allowed to cool in a flask, the mouth of which is closed by a plug of cotton wool. In this state it may be kept for weeks without crystallising, but on withdrawing the plug, crystallisation will be seen to commence at a few points on the surface immediately under the opening of the neck, and will spread slowly from these, octahedral crystals of alum of half an inch or more in diameter being built up in a few seconds, the temperature, at the same time, rising very considerably.

In the laboratory, stirring is always resorted to in order to induce crystallisation, if it does not take place spontaneously. Thus it is usual to test for potassium in a solution by adding tartaric acid, which should cause the formation of minute crystals of *hydro-potassium tartrate* (*cream of tartar*), but the test seldom succeeds unless the solutions are briskly stirred together with a glass rod. An amusing illustration of this is afforded by pouring a solution of tartaric acid into a solution of saltpetre, and allowing the clear mixture to run over a large plate of glass. Letters traced on the glass with the finger will now be rendered visible by the deposition of the crystals of the tartrate upon the glass.

39. The crystals of sodium sulphate produced in the above experiments contain, in a state of combination with the salt, more than half their weight of water. Their composition is—

Anhydrous sodium sulphate (Na_2SO_4)	142 parts,	or one molecule
Water	180 ,,	or ten molecules

as expressed by the formula $Na_2SO_4.10H_2O$. If some of the crystals be pressed between blotting-paper to remove adhering water, and left exposed to the air, they will gradually *effloresce*, or become covered with a white opaque powder. This powder is the anhydrous sodium sulphate into which the entire crystals would ultimately become converted by exposure to air. Since most crystals containing water have their crystalline form destroyed or modified by the loss of the water, it is commonly spoken of as *water of crystallisation*.

Coloured salts, containing water of crystallisation, generally change colour when the water is removed. The *sulphate of copper* (*blue stone*) affords an excellent example of this. The beautiful blue prismatic crystals of this salt contain—

Anhydrous sulphate of copper ($CuSO_4$)	159.5 parts,	or one molecule
Water	90 ,,	or five molecules

as expressed by the formula $CuSO_4.5H_2O$.

When these are exposed to the air at the ordinary temperature they remain unchanged; but if heated to the boiling point of water they become opaque, and may be easily crumbled down to a nearly white powder. This powder contains—

Anhydrous sulphate of copper ($CuSO_4$)	159.5 parts,	or one molecule
Water	18 ,,	or one molecule

and would therefore be represented by $CuSO_4.H_2O$. The four molecules of water, which have been expelled, constituted the water of crystallisation, upon which the form and colour of the sulphate of copper depend. If the white powder be moistened with water, combination takes place, with great evolution of heat, and the blue colour is reproduced. The one molecule of water which still remains is not expelled until the salt is heated to 390° F. (199° C.), proving that it is held to the sulphate of copper by a more powerful chemical attraction. On this account it is spoken of as *water of constitution*, and, in order that the formula of the salt may exhibit the difference between the water of constitution and of crystallisation, it is usually written $CuSO_4.H_2O.4Aq.$*

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* *Aqua*, water.

(DEFINITION.—*Water of crystallisation* of salts is that which is generally expelled at 212° F. (100° C.), and is connected with the form and colour of the crystals. *Water of constitution* is not generally expelled at 212° F., and is in more intimate connexion with the chemical properties of the salt.)

Several of the so-called *sympathetic inks* employed for writings which are invisible until heated, depend upon the change of colour which results from the loss of water of crystallisation. Characters written with a weak solution of chloride of cobalt and allowed to dry, are very nearly invisible, since the pink colour of so small a quantity of the salt is scarcely noticed; but on warming the paper, the pink hydrated chloride of cobalt ($CoCl_2.6Aq$) loses water of crystallisation, and the blue chloride with one molecule of water is produced. On exposure to air this again absorbs water, and the writing fades away.

Some salts have so great a tendency to combine with water that they become moist or *deliquesce* when exposed to air. This *deliquescence* is exhibited in a marked degree by *chloride of calcium*, and its great attraction for water is turned to advantage in drying air and other gases by passing them through tubes filled with the salt.

Nearly all salts appear to combine with water at very low temperatures; such compounds, which are decomposed at temperatures above 0° C., have been termed *cryo-hydrates* (*κρύος*, frost). Common salt combines with ice to form the cryo-hydrate $NaCl.10Aq$, which remains liquid down to $-20°$ C. Hence arises the use of crushed ice and salt as a freezing mixture, for just as ice alone, in melting, lowers the temperature to 0° C., the melting point of ice, so the compound of ice and NaCl, in melting, lowers the temperature to about $-20°$ C., the melting point of the cryo-hydrate.

40. Most bases are capable of combining with water to form hydrates, as exemplified in the slaking of lime. Anhydrous lime or quick-lime (CaO), when wetted with water, combines with it, evolving much heat, and crumbling to a loose bulky powder, which is hydrate of lime or slaked lime ($CaO.H_2O$). At a red heat the water is expelled, and anhydrous lime remains.

41. According to modern views, based upon the fact that several hydrates do not yield water when heated, the *hydrate of a metal* is defined as a compound formed by the replacement of a part of the hydrogen in water by a metal; thus potassium hydrate KHO is formed from water H_2O by the replacement of H by K; calcium hydrate $Ca(HO)_2$ is formed from two molecules of water $(H_2O)_2$ by the replacement of H_2 by (diatomic) calcium. The imaginary group HO, *hydroxyle*, would then be the *radical of the hydrates*, which are often termed *hydroxides*.

42. *Water from Natural Sources.*—Pure water is not found in nature. Rain is the purest form of natural water, but contains certain gases which it collects from the atmosphere during its fall. As soon as it reaches the earth it begins to dissolve small portions of the various solid materials with which it comes in contact, and thus becomes charged with salts and other substances to an extent varying, of course, with the nature of the soils and rocks which it has touched, and attaining its highest point in sea water, which contains a larger proportion of saline matters than water from any other natural source.

If a quantity of rain, spring, river, or sea water be boiled in a flask furnished with a tube also filled with the water, and passing under a gas cylinder standing in a trough of the same water (fig. 44), it will be found to give off a quantity of gas which was previously held in solution by the water, and is now set free because *gases are less soluble in hot than in cold water*. The quantity of this gas will vary according to the source of the water, but it will always be found to contain the gases existing in atmospheric air, viz., nitrogen, oxygen, and carbonic acid gas. One gallon of rain water will generally furnish about 4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic acid gas. It is worthy of remark, that the nitrogen and oxygen have been dissolved by the water, not in the proportions in which they exist in the atmosphere, but in the proportions in which they ought to be dissolved, if it be true that they exist in the air in the condition of mere mechanical admixture. The oxygen thus carried down from the air by rain appears to be serviceable in maintaining the respiration of aquatic animals, and in conferring upon river waters a self-purifying power, by acting upon certain organic matters which would probably prove hurtful to animals, and converting them into harmless products of oxidation. In the cases of rivers contaminated with the sewage of towns, this action of the dissolved oxygen is probably of great importance. The carbonic acid dissolved in rain water also probably serves some useful purposes in the chemical economy of nature. (See *Carbonic Acid.*)

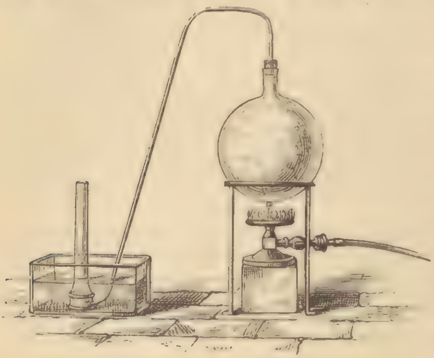

Fig. 44.

The *co-efficient of solubility* of a gas expresses the volume of gas absorbed by one volume of water. The numbers .02989 and .01478 respectively represent the volumes of oxygen and nitrogen absorbed by one volume of water, when exposed to the action of either gas, in a pure state, at 59° F. (15° C.). When a mixture of gases is brought into contact with water, the proportions in which the gases are absorbed can be ascertained by multiplying the co-efficient of solubility of each gas into its proportion by volume in the mixture. Thus, when water is exposed to air, containing $\frac{1}{5}$ volume of oxygen and $\frac{4}{5}$ volume of nitrogen, the quantities dissolved by one volume of water are,—

Oxygen . . . . $\frac{1}{5} \times .02989 = .00597$
Nitrogen . . . . $\frac{4}{5} \times .01478 = .01182$

or almost exactly two volumes of N to one volume of O.

43. The waters of wells, springs, and rivers, and especially those of the two first-named sources, differ very much from each other, according to the nature of the layers of rock or earth over or through which they have passed, and from which they dissolve a great variety of substances, some of which are familiar to us in daily life, while others are only met with in chemical collections. Under the former head may be enumerated Glauber's salt (sodium sulphate), common salt (sodium chloride), Epsom salt (magnesium sulphate), gypsum (calcium sulphate), chalk (calcium carbonate), common magnesia (magnesium carbonate), carbonic acid, and silica.

Among the substances known only to the chemist may be mentioned sulphuretted hydrogen, potassium sulphate, potassium chloride, calcium chloride, magnesium chloride, phosphates, bromides and iodides of calcium and magnesium (rarely), aluminium sulphate, carbonate of iron (ferrous carbonate), and certain vegetable substances.*

The well waters of certain localities (as, for example, those of large towns) also frequently contain salts of nitric and nitrous acids, and of ammonia.

The waters of springs and rivers do not differ very materially from well waters as to the nature of the substances which they contain, though, in the case of river waters more particularly, the quantity of these substances is materially influenced by the conditions of rapid motion and exposure to air under which such waters are placed.

Household experience has established a classification of the waters from natural sources into *soft* and *hard* waters—a division which depends chiefly upon the manner in which they act upon soap. If a piece of soap be gently rubbed in soft water (rain water, for example) it speedily furnishes a froth or *lather*, and its cleansing powers can be readily brought into action; but if a hard water (spring water) be substituted for rain water, the soap must be rubbed for a much longer time before a lather can be produced, or its effect in cleansing rendered evident; a number of white curdy flakes also make their appearance in the hard water, which were not seen when soft water was used. The explanation of this difference is a purely chemical one.

Soap is formed by the combination of a fatty acid with an alkali; it is manufactured by boiling oil or fat with potash or soda, the former for soft, the latter for hard soaps. In the preparation of ordinary hard soap, the soda takes from the oil or fat two acids,—*stearic* and *oleic* acid,—which exist in abundance in most varieties of fat, and unites with them to form soap, which in chemical language would be spoken of as a mixture of *stearate* and *oleate of sodium*.

If soap be rubbed in soft water until a little of it has dissolved, and some Epsom salts (magnesium sulphate) be dissolved in water, and poured into the soap water, curdy flakes will be produced, as when soap is rubbed in hard water, and the soap water will lose its property of frothing when stirred; the magnesium sulphate has decomposed the soap, forming sodium sulphate, which remains dissolved in the water, and insoluble curdy flakes, which consist of stearate and oleate of magnesium.

Similar to the effect of the magnesium sulphate is that of hard waters; their hardness is attributable to the presence of the different salts of calcium and magnesium, all of which decompose the soap in the manner exemplified above; the peculiar properties of the soap in forming a lather and dissolving grease can therefore be manifested only when a sufficient quantity has been employed to decompose the whole of the salts of calcium and magnesium contained in the quantity of water operated on, and thus a considerable amount of soap must be rendered useless when hard water is employed.

On examining the interior of a kettle in which spring, well, or river water has been boiled, it will be found to be coated more or less thickly with a *fur* or incrustation, generally of a brown colour, and the harder the water the more speedily will this incrustation be deposited. A chemical examination shows this deposit to consist chiefly of calcium carbonate in the form of minute crystals, which may be discovered by the microscope; it usually contains, in addition, some magnesium carbonate, calcium sulphate, and small quantities of oxide of iron (rust) and vegetable matter, the last two substances imparting its brown colour. In order to explain the formation of this deposit, it is necessary to become acquainted with the particular condition in which the calcium carbonate exists in natural waters; it is hardly dissolved to any perceptible extent by pure water, though it may be dissolved in considerable quantity by carbonic acid. This statement, which is of great importance in connexion with natural waters, may be verified in the following manner: a little slaked lime is well shaken up in a bottle of distilled or rain water, which is afterwards set aside for an hour or two; as soon as that portion of the lime which has not been dissolved has subsided, the clear portion is carefully poured into a glass, and a little soda water or solution of carbonic acid in water is added to it; the first addition of the carbonic acid to the lime water causes a milkiness, due to the formation of minute particles of calcium carbonate; this being insoluble in the water, separates from it, or *precipitates*, and impairs the transparency of the liquid; a further addition of carbonic acid water renders the liquid again transparent, for the carbonic acid dissolves the calcium carbonate which has separated.

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* Although it is certainly known that the acids and bases capable of forming the salts here enumerated may be detected in spring and river waters, their exact distribution amongst each other is still a matter of uncertainty.

If this clear solution be introduced into a flask, and boiled over the spirit-lamp or gas-flame, it will again become turbid, for the free carbonic acid will be expelled by the heat, and the calcium carbonate will be deposited, not now, however, in so fine a powder as before, but in small, hard grains, which have a tendency to fix themselves firmly upon the sides of the flask, and, when examined by the microscope, are seen to consist of small crystals.

In a similar manner, when natural waters are boiled, the carbonic acid gas which they contain is expelled, and the carbonates of calcium, magnesium, and iron are precipitated, since they are insoluble in water which does not contain carbonic acid. But, by the ebullition of the water, a portion of it has been dissipated in vapour, and if there be much calcium sulphate present, the quantity of water left may not be sufficient to retain the whole of the salt in solution; calcium sulphate requires about 500 parts of cold water to dissolve it, and is nearly insoluble in water having a higher temperature than 212° F., as would be the case in boilers worked under pressure, so that it would readily be deposited. It contributes much to the formation of compact incrustations. Should the water contain much vegetable matter, this is often deposited in an insoluble condition, the whole eventually forming together a hard compact mass, composed of successive thin layers, on the bottom and sides of the vessel in which the water has been boiled. The "furring" of a kettle is objectionable, chiefly in consequence of its retarding the ebullition of the water, since the deposit is a very bad conductor of heat, and therefore impedes the transmission of heat from the fire to the water; hence the common practice of introducing a round stone or marble into the kettle, in order, by its perpetual rolling, to prevent the particles of calcium carbonate from forming a compact layer. In steam boilers, however, even more serious inconvenience than loss of time sometimes arises if this deposit be allowed to accumulate, and to form a thick layer of badly conducting material on the bottom of the boiler, since the latter is then liable to become red hot, and should the incrustation happen to crack, and allow the water to reach the red hot metal, so violent a disengagement of steam follows, that boilers have been known to burst under the sudden pressure. But even though this calamity be escaped, the wear and tear of the boiler is very much increased in consequence of the formation of this deposit, since its hardness often renders it necessary to detach it with the hammer, much to the injury of the iron boiler-plates, which are also subject to increased oxidation and corrosion in consequence of the high temperature which the incrustation permits them to attain by preventing their contact with the water. Many propositions have been brought forward for the prevention of these incrustations; some substances have been used, of which the action appears to be purely mechanical, in preventing the aggregation of the deposited particles. Clay, sawdust, and other matters have been employed with this view; but the action of sal ammoniac (ammonium chloride), which has also been found efficacious, must be explained upon purely chemical principles. When this salt is boiled with calcium carbonate, mutual decomposition ensues, resulting in the production of calcium chloride and ammonium carbonate, of which salts the former is very soluble in water, while the latter passes off in vapour with the steam. The ammonium chloride, however, corrodes the metal of the boiler. Solutions of the caustic alkalies, of alkaline carbonates, arsenites, tannates, &c., are also occasionally employed to prevent the formation of incrustations in boilers, and probably act by precipitating calcium carbonate and other calcium compounds which act as *nuclei*, around which the *fur* collects as a loose deposit or *mud*.

The deposit formed in boilers fed with sea water consists chiefly of calcium sulphate and magnesium hydrate, the latter resulting from the decomposition of the magnesium chloride present in sea water.

The incrustations formed in cisterns and pipes by hard water are also produced by the carbonates of calcium and magnesium deposited in consequence of the escape of the free carbonic acid which held them in solution. Many interesting natural phenomena may be explained upon the same principle. The so-called *petrifying springs*, in many cases, owe their remarkable properties to the considerable quantity of calcium carbonate dissolved in carbonic acid which they contain; when any object, a basket, for example, is repeatedly exposed to the action of these waters, it becomes coated with a compact layer of the carbonate, and thus appears to have suffered conversion into limestone. The celebrated waters of the Sprudel at Carlsbad, of San-Filippo in Tuscany, and of Saint Allyre in Auvergne are the best instances of this kind.

The *stalactites* and *stalagmites*,[*] which are formed in many caverns or natural grottoes (fig. 45), afford beautiful examples of the gradual separation of calcium carbonate from water charged with carbonic acid.

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[*] From *σταλάζω, to drop; στάλαγμα, a drop.*

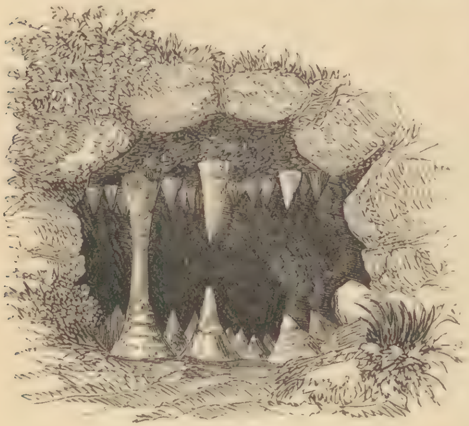

Fig. 45.—Stalactite cavern.

Each drop of water, as it trickles through the roof of the cavern, becomes surrounded with a shell of calcium carbonate, the length of which is prolonged by each drop as it falls, till a stalactite is formed, varying in colour according to the nature of the substances which are separated from the water together with the carbonate (such as the oxides of iron and vegetable matter); and as each drop falls from the point of the stalactite upon the floor of the cavern, it deposits there another shell, which grows, like the upper one, but in the opposite direction, and forms a stalagmite, thus adorning the grotto with conical pillars of calcium carbonate, sometimes, as in the case of the *oriental alabaster*, variegated with red and yellow, and applicable to ornamental purposes.

When water which has been boiled for some time is compared with unboiled water from the same source, it will be found to have become much softer, and this can now be easily explained, for, a considerable portion of the salts of calcium and magnesium having separated from the water, the latter is not capable of decomposing so large a quantity of soap. The amount of hardness which is thus destroyed by boiling is generally spoken of as *temporary* hardness, to distinguish it from the *permanent* hardness due to the soluble salts of calcium and magnesium which still remain in the boiled water. It is customary with analytical chemists, in reporting upon the quality of natural waters, to express the hardness by a certain number of degrees which indicate the number of grains of chalk or carbonate of calcium which would be dissolved in a gallon of water containing carbonic acid, in order to render its hardness equal to that of the water examined, that is, to render it capable of decomposing an equal quantity of soap. Thus, when a water is spoken of as having 16 degrees of hardness, it is implied that 16 grs. of calcium carbonate dissolved in a gallon of water containing carbonic acid, would render that gallon of water capable of decomposing as much soap as a gallon of the water under consideration.

The utility of a water for household purposes must be estimated, therefore, not merely according to the total number of degrees of hardness which it exhibits, but also by the proportion of that hardness which may be regarded as temporary, that is, which disappears when the water is boiled. Thus, the total hardness of the New River water amounts to nearly 15 degrees, that of the Grand Junction Company to 14 degrees, and yet these waters are quite applicable to household uses, since their hardness is reduced by boiling to about 5 degrees. It has been ascertained that every degree of hardness in water gives rise to a waste of about 10 grs. of soap for every gallon of water employed, and hence the use of 100 gallons of Thames or New River water in washing will be attended with the loss of about 2 lbs. of soap; this loss is reduced, however, to about one-third when the temporary hardness has been destroyed by boiling. The addition of washing soda (sodium carbonate) removes not only the temporary, but also the permanent hardness due to the presence of the sulphates of calcium and magnesium in the water, for both these salts are decomposed by the sodium carbonate which separates the calcium and magnesium as insoluble carbonates, while sodium sulphate remains dissolved in the water.* The household practice of boiling the water, and adding a little washing soda, is therefore very efficacious in removing the hardness. *Clark's process* for softening waters depends upon the neutralisation of the free carbonic acid contained in the water by the addition of a certain quantity of lime; the calcium carbonate so produced separates together with the carbonates of calcium and magnesium, which were previously retained in solution by the free carbonic acid; this process, therefore, affects chiefly the temporary hardness; moreover, the earthy carbonates which are separated appear to remove from the water a portion of the organic matter which it contains, and thus effect a very important purification. The water under treatment is mixed, in large tanks, with a due proportion of lime or lime-water (the quantity necessary having been determined by preliminary experiment), and the mixture allowed to settle until perfectly clear, when it is drawn off into reservoirs.† A modern improvement in the process (*Porter-Clark process*) consists in separating the deposit by a remarkably expeditious filtration, which dispenses with much of the tank-space required by the original process.

Waters which are turbid from the presence of clay in a state of suspension, are sometimes purified by the addition of a small quantity of alum or of aluminium sulphate, when the alumina is precipitated by the calcium carbonate, and carries down with it mechanically the suspended clay, leaving the water clear.

The *organic matter* contained in water may be vegetable matter dissolved from the earth with which it has come in contact, or resulting from the decomposition of plants, or it may be animal matter derived either from the animalcules and fish naturally existing in it, or from the sewage of towns, and, in the case of well waters, from surface drainage.

It is believed upon good medical authority, that cholera, diarrhœa, and typhoid fever are propagated by certain *spores* or *germs*, which are present in the evacuations of persons suffering from those maladies, and are conveyed into water which is allowed to become contaminated by sewage.

On this account, much attention is paid, in the analysis of water intended for drinking, to the detection of organic matters containing nitrogen (so-called *albuminoid* matters) which would be conveyed into the water in sewage. The analytical operations necessary for this pur-

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* $$\underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

† Thames and New River water are softened, in this way, to 3.5, or to a lower point than by an hour's boiling.

pose require great care and skill, and the conclusions to be drawn from their results are by no means finally agreed upon among scientific chemists.

There are, however, certain simple tests, which may often determine whether it is worth while to undertake a more elaborate examination of the water.

1. Pour half a pint of the water into a wide-mouthed bottle or decanter, close it with the stopper or with the palm of the hand, and shake it violently up and down. If an offensive odour is then perceived, the water is probably contaminated by sewage-gas, and possibly with other constituents from the same source.

2. Add to a little of the water a drop or two of dilute sulphuric acid, and enough potassium permanganate (*Condy's red fluid* or *ozonised water*) to tinge it of a faint rose colour; cover the vessel with a glass plate or a saucer. If the pink tinge be still visible after the lapse of a quarter of an hour, the water is probably wholesome.

3. Pour a little solution of silver nitrate (*lunar caustic*) into a carefully *cleaned glass*, and see that it remains transparent; then pour in some of the water; should a *strong* milkiness appear, which is not cleared up on adding a little diluted nitric acid, the water probably contains much sodium chloride, which is always found in sewage-water, but seldom in wholesome waters in any large quantity, unless near the sea-coast.

To render an impure water fit to drink, a chemist would naturally recommend distillation, but in many cases this is impracticable, and the consumer may protect himself to a great extent by boiling the water, or by filtering it through charcoal or *spongy* iron, or by applying Clark's process, or treating it with alum (p. 51).

44. One of the most important points to be taken into account in estimating the qualities of a water is its action upon lead, since this metal is unfortunately so generally employed for the storage and transmission of water, and cases frequently occur in which the health has been seriously injured by repeated small doses of compounds of lead taken in water which has been kept in a leaden cistern. If a piece of bright freshly scraped lead be exposed to the air, it speedily becomes tarnished from the formation of a thin film of the oxide of lead, produced by the action of the atmospheric oxygen; this oxide of lead is soluble in water to some extent, and hence, when lead is kept in contact with water, the oxygen which is dissolved in it acts upon the metal, and the oxide so produced is dissolved by the water; but fortunately, different waters act with very different degrees of rapidity upon the metal, according to the nature of the substances which they contain.

The film of oxide which forms upon the surface of the lead is insoluble, or nearly so, in water containing much sulphate or carbonate of calcium, so that hard waters may generally be kept without danger in leaden cisterns, but soft waters, and those which contain nitrites or nitrates, should not be drunk after contact with lead. Nearly all waters which have been stored in leaden cisterns contain a trace of the metal, and since the action of this poison, in minute doses, upon the system is so gradual that the mischief is often referred to other causes, it is much to be desired that lead should be discarded altogether for the construction of cisterns. (See *Lead*.)

To detect lead in a water, fill a glass tumbler with it, place this on white paper, add a drop or two of diluted nitric acid, and some hydrosulphuric acid; a dark brown tinge will be seen on looking through it from above.

Mineral waters, as they are popularly called, are simply spring waters containing so large a quantity of some ingredient as to have a decided medicinal action. They are differently named according to the nature of their predominating constituent. Thus, a *chalybeate* water contains a considerable quantity of a salt of iron (usually ferrous carbonate dissolved by free carbonic acid); an *acidulous* water is distinguished by a large proportion of carbonic acid, and is well exemplified in the celebrated Seltzer water; a *sulphureous* or *hepatic* water has the nauseous odour due to the presence of sulphuretted hydrogen. The Harrogate water is eminently sulphureous. *Saline* waters are such as contain a large quantity of some salt; thus the saline springs of Cheltenham are rich in common salt and sodium sulphate.

The chalybeate waters, which are by no means uncommon, become brown when exposed to the air, and deposit a rusty sediment which consists of the ferric hydrate, formed by the action of the oxygen of the air on the carbonate. (See *Iron*.)

45. *Sea water* contains the same salts as are found in waters from other natural sources, but is distinguished by the very large proportion of sodium chloride (common salt). A gallon of sea water contains usually about 2500 grains of saline matter, of which 1890 grains consist of common salt. The circumstance that clothes wetted with sea water never become perfectly dry is to be ascribed chiefly to the *magnesium chloride* present in the water, which is distinguished by its tendency to *deliquesce* or become damp in moist air. There are two elements, *bromine* and *iodine*, which are found combined with metals in appreciable quantity in sea water, though they are of somewhat rare occurrence in other waters derived from natural sources.

46. By *distillation* pure water may be obtained from most spring and river waters.

(Definition.—*Distillation* is the conversion of a liquid into a vapour, and its re-condensation into the liquid form in another vessel.)

Fig. 46 represents the ordinary form of still in common use, in which A is a copper boiler containing the water to be distilled; B the *head* of the still, which lifts out at *b*, and is connected by the neck C with the *worm* D, a tin pipe coiled round in the tub E, and issuing at F. The steam from the boiler, passing into the worm, is condensed to the liquid state, being cooled by the water in contact with the worm; this water, becoming heated, passes off through the pipe G, being replaced by cold water, which is allowed to enter through H.* If 10 gallons of river water be taken, 8½ may be distilled over, but the first half gallon should be collected separately, as it contains ammonia and carbonic acid.

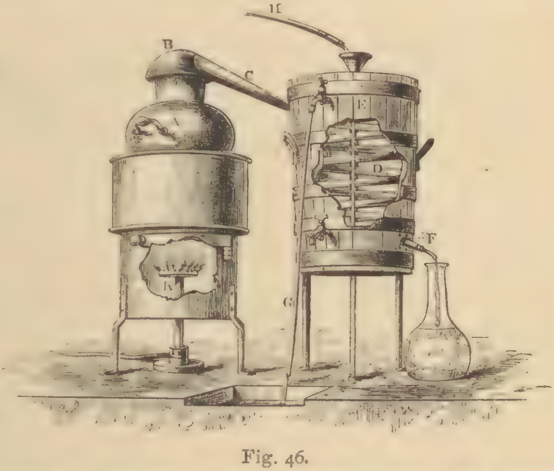

Fig. 46.

Another form of apparatus for distillation of water and other liquids is shown in fig. 47. A is a stoppered *retort*, the neck of which fits into the tube of a *Liebig's condenser* (B), which consists of a glass tube (C) fitted by means of corks into a glass, copper, or tinned iron tube D, into which a stream of cold water is passed by the funnel E, the heated water running out through the upper tube F.

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* A rosette gas-burner (K) on Bunsen's principle is very convenient for a small still of this description.

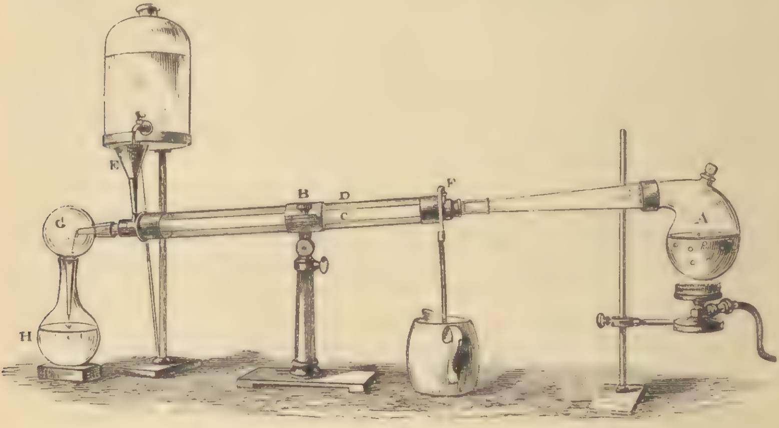

Fig. 47.—Distillation—Liebig's condenser.

The water furnished by the condensation of the steam passes through the *quilled receiver* G, into the flask H. Heat is gradually applied to the retort by a ring gas-burner.

Many special precautions are requisite in order to obtain absolutely pure distilled water for refined experiments, but for ordinary purposes the common methods of distillation yield it in a sufficiently pure condition.

The saline matters present in the water are of course left behind in the still or retort. Sea water is now frequently distilled on board ship when fresh water is scarce. The vapid and disagreeable taste of distilled water, which is due to its having been deprived of the dissolved air during the distillation, is remedied by the use of *Normandy's still*, which provides for the restoration of the expelled air.

47. The physical properties of water are too well known to require any detailed description. Its specific gravity in the liquid state is = 1. being taken as the standard to which the specific gravities of liquid and solid bodies are referred.

(Definition.—The *specific gravity of a liquid or solid body* is its weight as compared with that of an equal volume of pure water at 60° F., 15°.5 C.)

Water assumes the solid form, under ordinary circumstances, at 32° F. (0° C.), and may be obtained in six-sided prismatic crystals. Snow consists of beautiful stellate groupings of these crystals. Ice has the specific gravity 0.9184. In the act of freezing, water expands very considerably, so that 174 volumes of water at 60° F. become 184 volumes of ice. The breakage of vessels, splitting of rocks, &c., by the congelation of water are due to this expansion. Water passes off in vapour at all temperatures, the amount of vapour evolved in a given time of course increasing with the temperature. The boiling point of water is 212° F. (100° C.). Its *absolute* boiling point is 1076° F. (580° C.).

(DEFINITION.—The *boiling point* of a liquid is the constant temperature indicated by a thermometer, immersed in the vapour of the boiling liquid, in the presence of a coil of platinum wire, to facilitate disengagement of vapour, and at a pressure of 30 in. (762 mm.) Bar.)

The absolute boiling point of a liquid is that temperature above which it cannot exist in the liquid state, whatever the pressure.

At and above 212° F. at the ordinary atmospheric pressure (30 in. Bar.), water is an invisible vapour of specific gravity 0.622 (air = 1). One cubic inch of water at 60° F. becomes 1696 cubic inches of vapour at 212° F.

Since the specific gravity of a gas or vapour is the weight of one volume (p. 19), and the molecule of a compound gas occupies two volumes, *the specific gravity of a compound gas or vapour, referred to hydrogen as the standard, is the half of its molecular weight.*

Thus the molecular weight of steam being 18, its specific gravity ($H = 1$) would be 9.

If the specific gravity in relation to air be required, it may be obtained by multiplying half the molecular weight by 0.0692, which represents the specific gravity of hydrogen referred to air as the unit. Thus the specific gravity of steam (air = 1) is $9 \times 0.0692 = .6228$.

48. *Peroxide of hydrogen* or *hydric peroxide*. H_2O_2, sometimes called *hydroxyle* $(HO)_2$. This compound is seldom met with in nature, and has no very important useful application in the arts, but it possesses very great interest for the student of chemical philosophy, because it helps to throw some light upon the molecular constitution of the elements.

To prepare the hydric peroxide, some baryta (BaO) is heated in a current of oxygen, when it becomes converted into the barium dioxide (BaO_2). If this be powdered, suspended in water, and gradually added to water through which is passing a stream of carbonic acid gas, the water becomes charged with the hydric peroxide; $BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2$. The barium carbonate is allowed to subside, and the clear solution of hydric peroxide poured off.

To prepare pure hydric peroxide, some barium dioxide (BaO_2) is heated to the temperature at which it begins to evolve oxygen, and dissolved in as little diluted nitric acid as possible. To this solution one of barium hydrate (baryta water) is added; the precipitate, $BaO_2.8H_2O$, is washed by decantation, and gradually added to diluted sulphuric acid (1 acid to 6 water, by weight), care being taken to leave the liquid *very slightly* acid, $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. The precipitate is allowed to subside, and the clear liquid evaporated in the exhausted receiver of the air-pump over a dish of oil of vitriol to absorb the water, which evaporates much more rapidly than the peroxide. The pure hydric peroxide is a syrupy liquid of sp. gr. 1.453, with a very slight chlorous odour. Its most remarkable feature is the facility with which it is decomposed into water and oxygen.* Even at 70° F. it begins to evolve bubbles of oxygen. At 212° it decomposes with violence. The mere contact with certain metals, such as gold, platinum, and silver, which have no direct attraction for oxygen, will cause the decomposition of the peroxide without any chemical alteration of the metal itself.† Manganese dioxide decomposes it without undergoing any apparent change. The most surprising effect is that which takes place with silver oxide. If a drop of hydric peroxide be allowed to fall upon silver oxide, which is a brown powder, decomposition takes place with explosive violence and great evolution of heat, the silver oxide losing its oxygen, and becoming grey metallic silver.* The oxides of gold and platinum are acted upon in a similar manner.

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* The presence of a little free acid renders it rather more stable, whilst free alkali has the opposite effect. A solution of hydric peroxide, containing a little hydrochloric acid, is now sold for medicinal and photographic uses.

† Such inexplicable changes as this are sometimes included under the general denomination of *catalysis*, or decomposition by contact.

These very extraordinary changes, which were formerly described as *catalytic actions*, are now generally accounted for by the hypothesis that the oxygen in the oxide of silver, &c., exists in a condition different from that of the second atom of oxygen in the hydric peroxide, and that these two conditions of oxygen have a chemical attraction for each other, similar to that which exists between different elements. If the oxygen in the silver oxide be represented as *electro-negative* oxygen (see 2), as its relation to the metal would lead us to expect, and the second atom of oxygen in the hydric peroxide be represented as *electro-positive* oxygen, the mutual decomposition of the two compounds might be represented by the equation,

$$Ag_2\overset{-}{O} + H_2O\overset{+}{O} = Ag_2 + H_2O + \overset{-}{O}\overset{+}{O}.$$

The elementary substances, with few exceptions, have molecules composed of two atoms, which may be due to the circumstance that each atom is the electrical complement of the other.

If hydric peroxide, even in diluted solution, be added to potassium permanganate acidified with sulphuric acid, the red colour is entirely destroyed, and bubbles of oxygen are evolved, causing effervescence; $K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. Here O_5 from the hydric peroxide have united with O_5 from the permanganate.

These experiments support the conclusion arrived at by the reasoning at page 2, that the molecule or ultimate physical particle of oxygen is really composed of 2 atoms.

A very striking reaction of hydric peroxide is that with chromic acid. If a solution of H_2O_2 be added to a weak solution of potassium dichromate acidified with sulphuric acid, the beautiful blue colour of perchromic acid appears: $K_2Cr_2O_7 + H_2SO_4 + 2H_2O_2 = K_2SO_4 + 3H_2O + H_2Cr_2O_8$. After a few minutes, the blue colour changes to a very pale green, the perchromic acid being decomposed by the sulphuric acid, yielding the green chromium sulphate, and free oxygen which adheres in bubbles to the side of the vessel, $H_2Cr_2O_8 + 3H_2SO_4 = Cr_2(SO_4)_3 + 4H_2O + O_4$. If the blue solution be shaken with a little ether which dissolves the perchromic acid and rises with it to the surface where it forms a blue layer, the colour is much more lasting, and very minute quantities of hydric peroxide may thus be detected.

The decomposition of H_2O_2 into H_2O and O is attended by evolution of heat, amounting to 22000 grm.-units of heat for each grm.-molecule of H_2O_2. When H_2 and O combine to form H_2O, 69000 units of heat are evolved; hence, when H_2O is decomposed, 69000 units must be absorbed, so that we have, in the formation of water, $H_2 + O = H_2O + 69000$ heat-units. But since the decomposition of H_2O_2 into H_2O and O evolves 22000 units, its formation from H_2O and O would absorb the same quantity, and we should have $H_2O + O = H_2O_2 - 22000$ units. From the two equations we get $H_2 + O_2 = H_2O_2 + 69000 - 22000$, or $H_2 + O_2 = H_2O_2 + 47000$ heat-units. Now, by the laws of thermo-chemistry, *every chemical change tends to produce that body in the formation of which most heat is liberated*: hence water, and not hydric peroxide, is the general result of chemical changes in which H and O are concerned.

49. OZONE.—This is the name given to a modified form of oxygen, of the true nature of which there is still some doubt, as it has never been obtained unmixed with ordinary oxygen, but it appears to be formed by the union of 3 atoms of oxygen (occupying 3 volumes), to produce a molecule of ozone (occupying 2 volumes). Just as hydric peroxide (H_2O_2) may be regarded as formed by the combination of a molecule of water (H_2O) with an atom of oxygen, so ozone may be viewed as a combination of a molecule of oxygen (O_2) with an atom of oxygen. It would then be half as heavy again as ordinary oxygen, and experiment has shown that its rate of diffusion is in accordance with this view.

It derives its name from its peculiar odour (*ὄζειν, to smell*), which is often perceived in the air of the sea or of the open country, and in linen which has been dried in country air. According to Hartley, 1 volume of ozone in 2½ million vols. of air may be perceived by the smell. Oxygen appears to be capable of assuming this *ozonised* condition under various circumstances, the principal of which are, the passage of silent electric discharges,* and the contact with substances (such as phosphorus) undergoing slow oxidation in the presence of water. A minute proportion of the oxygen obtained in the decomposition of water by the galvanic current also exists in the ozonised condition, as may be perceived by its odour.

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* If ammonia be very carefully added to silver nitrate until the precipitate formed at first is only just re-dissolved, the solution will give a lustrous deposit of metallic silver on addition of a little hydric peroxide, and gently heating.

The use of Siemens' induction-tube (fig. 48) affords the readiest method of demonstrating the characteristic properties of ozone. This apparatus consists of a tube (A) coated internally with tin-foil (or silvered on the inside), and surrounded with another tube (B), which is coated with tin-foil on the outside. When the inner and outer coatings are placed in connexion with the wires of an induction-coil by means of the screws (CD), and a stream of air or oxygen (dried by passing through oil of vitriol) is passed through (E) between the two tubes, a strong odour is perceived at the orifice (F).

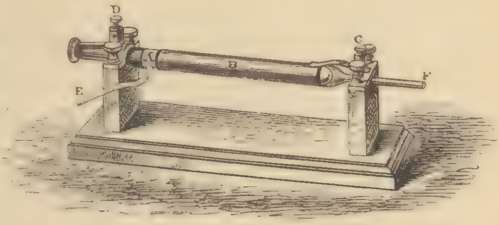

Fig. 48.—Tube for ozonising air by induction.

Several forms of apparatus upon this principle have been constructed for obtaining large volumes of ozonised air. Plates of glass coated with tin-foil will ozonise the air between them when the coatings are connected with opposite poles of the induction-coil. A wide glass tube or cylinder with a platinum wire, or a piece of platinum foil inside, connected with one pole of the coil, and a platinum wire wound round it externally, connected with the other pole of the coil, will ozonise the air passed through it. When large quantities of ozone are required, it is found expedient to employ concentric cylinders filled with water, or diluted sulphuric acid, which serves to keep down the temperature, and may be employed, instead of a metallic coating, to receive the charge of electricity (fig. 49).

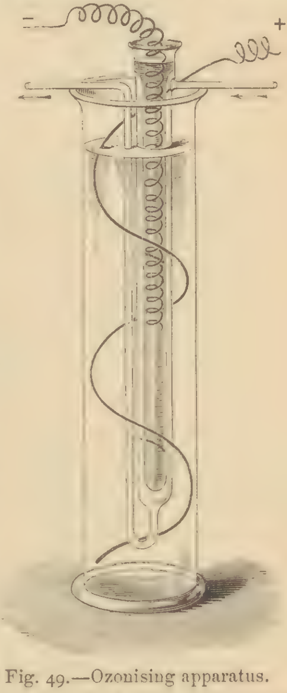

Fig. 49.—Ozonising apparatus.

The ordinary chemical test for ozone is a damp mixture of starch with potassium iodide. 100 grains of starch are well mixed in a mortar with a measured ounce of cold water, and the mixture is slowly poured into 5 ounces of boiling water in a porcelain dish, with occasional stirring. The thin starch-paste thus obtained is allowed to cool, and a few drops of solution of pure potassium iodide are added, the mixture being well stirred with a glass rod. If this mixture be brushed over strips of white cartridge paper, these will remain unchanged in ordinary air; but when they are exposed to ozonised air (such as that which has passed through the induction-tube), they will immediately assume a blue colour. The ozone abstracts the potassium from the potassium iodide (KI), and sets free the iodine, which has the specific property of imparting a blue colour to starch. Papers impregnated with manganese sulphate or lead acetate become brown from the formation of the peroxides of those metals under the influence of ozone.

If the ozonised air issuing from F be passed into a solution of indigo (*sulphindigotic acid* largely diluted) the blue colour will soon disappear, since the ozone oxidises the indigo, and gives rise to products which, in a diluted state, are nearly colourless. Ordinary oxygen is incapable of bleaching indigo in this manner. If the ozone is passed through a tube of vulcanised caoutchouc, this will soon be perforated by the corrosive effect of the ozone, whilst ordinary oxygen would be without effect upon it. If ozonised air be passed into a flask with a little mercury at the bottom, the surface of the mercury will soon become tarnished by the formation of oxide, and when the mercury is shaken round the flask it will adhere to the sides, which is not the case with pure mercury.

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* It is the odour of ozone which is perceived in working an ordinary electrical machine.

If the ozone from F be made to pass slowly through a glass tube heated in the centre by a spirit-lamp, it will be found to lose its power of affecting the iodised starch-paper, the ozone having been reconverted into ordinary oxygen under the influence of heat ; $2(OO_2) = 3(O_2)$. A temperature of 300° F. (149° C.) is sufficient to effect this change. A given volume of oxygen diminishes when a portion of it is converted into ozone by the silent electric discharge, and it regains its original volume when the ozone is reconverted by heat. The conversion of oxygen into ozone is attended by absorption of heat ; $3O_2 = 2O_3 - 29600$ units.

When a given quantity of oxygen is *electrised*, or subjected to the action of surfaces charged with opposite electricities, only one-fifth, at most, is converted into ozone ; but if the ozone be now removed by some substance which absorbs it, a fresh quantity of the oxygen may be ozonised.

The researches of Brodie have shown that either one, two, or three atoms of oxygen in ozone may be absorbed, according to the nature of the oxidisable substance employed. Thus, where a neutral solution of potassium iodide is acted on by ozone,

$$OO_2 \text{ (2 volumes)} + 2KI + H_2O = 2KHO + I_2 + O_2 \text{ (2 volumes)},$$

the atom of oxygen being removed without diminution in the volume of the gas. But if the solution of potassium iodide be acidified (and thus converted, virtually, into a solution of hydriodic acid),

$$OO_2 \text{ (2 volumes)} + 4HI = 2H_2O + I_4 + O \text{ (1 volume)},$$

the volume being here reduced by one-half. When chloride of tin (stannous chloride) mixed with hydrochloric acid is brought in contact with ozone, the latter is entirely absorbed, converting the stannous chloride into stannic chloride.

$$OO_2 + 3SnCl_2 + 6HCl = 3SnCl_4 + 3H_2O.$$

Oil of turpentine and some other substances also absorb the ozone entirely.

By placing a freshly scraped stick of phosphorus (scraped under water to avoid inflammation) at the bottom of a quart bottle, with enough water to cover half of it, and loosely covering the bottle with a glass plate, enough ozone may be accumulated in a few minutes to be readily recognised by the odour and the iodised starch.

The water at the bottom of the bottle is found to contain, besides the phosphorus and phosphoric acids, formed by the slow oxidation of the phosphorus, some hydric peroxide, whence it has been supposed that the formation of ozone is due to the decomposition of a molecule of oxygen into electro-negative oxygen, which combines with another molecule of oxygen to form ozone, and electro-positive oxygen which combines with a molecule of water to form hydric peroxide. Thus,

$$O_2 + \overset{-}{O}\overset{+}{O} + H_2O = H_2O\overset{+}{O} + O_2\overset{-}{O}.$$

This view is supported by the circumstance that hydric peroxide appears to be produced in every case where ozone is formed in the presence of water.

When ozonised oxygen is shaken with hydric peroxide, the above equation is reversed, water and ordinary oxygen resulting.*

Ether and essential oils, such as turpentine, slowly absorb oxygen from the air, thus acquiring the property of bleaching indigo and of blueing the mixture of potassium iodide and starch ; hence they were formerly believed to contain ozone, but they do not answer to all the tests for that substance. Thus ozone imparts a blue colour to the resin of *guaiacum*, but the old turpentine or ether will not do so.† If a little hydric peroxide be dissolved in ether, it exhibits the same property as the ether which has absorbed oxygen from the air, and it is, therefore, sometimes called "*ozonic ether*." The solution of hydric peroxide in ether

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* The oxygen obtained by the action of warm sulphuric acid on barium dioxide or on crystallised potassium permanganate, resembles ozone in its odour and action on the iodised starch paper.

† Kingzett has shown that the action of air on oil of turpentine produces an organic substance which yields hydric peroxide when acted on by water. (See *Turpentine*.)

(obtained by shaking the aqueous solution of the peroxide with ether) is employed by Dr. Day for the recognition of blood-stains. Contact with blood decomposes hydric peroxide, and the oxygen which is liberated is capable of blueing guaiacum resin. Accordingly, if a blood-stain be moistened with tincture of guaiacum (a solution of the resin in spirit of wine), and afterwards with the ethereal solution of hydric peroxide (ozonic ether), it acquires an intense blue colour, which may be detected, even on a coloured fabric, by pressing a piece of white blotting-paper upon it.

Ozone has attracted much notice, because a minute proportion of the oxygen in the atmosphere appears sometimes to be present in this form, and its active properties have naturally led to the belief that it must exercise some influence upon the sanitary condition of the air. This idea is encouraged by the circumstance that no indications of ozone can be perceived in crowded cities, where there are so many oxidisable substances to consume the active oxygen, whilst the air in the open country and at the sea-side does give evidence of its presence. Some chemists assert that their experiments have demonstrated the very important fact that a portion of the oxygen developed by growing plants is in the ozonised form, but the evidence on the subject is conflicting. Houzeau fixes the maximum proportion of ozone at $\frac{1}{700000}$th of the volume of air. The proportion is highest in May and June, lowest in December and January.

Ozonised oxygen exhibits a sky-blue colour when viewed along a column of one metre in length. The blue colour becomes very deep under a pressure of several atmospheres. It has been suggested that the blue colour of the sky is due to our regarding it through the ozonised atmosphere.* Ozone is more easily liquefied than oxygen, being condensed to a blue liquid by a pressure of 125 atmospheres at − 105° C. It is slightly soluble in water; 100 vols. water dissolve .88 vol. ozone.

In want of stability, ozone resembles hydric peroxide; contact with manganese dioxide converts it into ordinary oxygen. Even shaking with powdered glass will de-ozonise the ozonised oxygen. When kept for some days, all the ozone is gradually reconverted into oxygen.

ATMOSPHERIC AIR.

50. Atmospheric air consists chiefly of a mixture of nitrogen with one-fifth of its volume of oxygen, and very small proportions of carbonic acid gas and ammonia. Vapour of water is of course always present in the atmosphere in varying proportions. Since the atmosphere is the receptacle for all gaseous emanations, other substances may be discovered in it by very minute analysis, but in proportions too small to have any perceptible influence upon its properties. Thus marsh-gas or light carburetted hydrogen, sulphuretted hydrogen, and sulphurous acid gas, can often be traced in it, the two last especially in or near towns.

Although the proportion of oxygen in the air at a given spot may be much diminished, and that of carbonic acid gas increased, by processes of oxidation (such as respiration and combustion) taking place there, the operation of wind and of diffusion so rapidly mixes the altered air with the immensely greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight. Thus it has been found that the proportion of oxygen in the air in the centre of Manchester was, at most, only 0.2 per cent. below the average.

The proportions in which the oxygen and nitrogen are generally present in atmospheric air, freed from water and carbonic acid gas, are—nitrogen, 79.19 per cent. by volume, or 76.99 per cent. by weight; oxygen, 20.81 per cent. by volume, or 23.01 per cent. by weight.

The proportion of aqueous vapour may be stated, on the average, as 1.4 per cent. by volume, or 0.87 per cent. by weight of the air. The carbonic acid gas may be generally estimated at from 0.03 to 0.04 per cent. by volume, or from 0.045 to 0.06 per cent. by weight of the air. The total weight of atmospheric air surrounding the globe exceeds 300,000 million tons.

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* "On the Absorption of Solar Rays by Atmospheric Ozone," Hartley, *Journ. Chem. Soc.*, March 1881.

The relative proportions of oxygen and nitrogen in air may be exhibited by suspending a stick of phosphorus upon a wire stand (A, fig. 50) in a measured volume of air confined over water. The cylinder (B) should have been previously divided into five equal spaces by measuring water into it, and marking each space by a thin line of Brunswick black. After a few hours, the phosphorus will have combined with the whole of the oxygen to form phosphorous and phosphoric acids, which are absorbed by the water, leaving four of the spaces occupied by nitrogen.

The same result may be arrived at in a much shorter time by burning the phosphorus in the confined portion of air.

A fragment of phosphorus dried by careful pressure between blotting-paper, is placed upon a convenient stand (A, fig. 51) and covered with a tall jar, having an opening at the top for the insertion of a well-fitting stopper (which should be greased with a little lard), and divided into seven parts of equal capacity. The jar should be placed over the stand in such a manner that the water may occupy the two lowest spaces into which the jar is divided. The stopper of the jar is furnished with a hook, to which a piece of brass chain (B) is attached, long enough to touch the phosphorus when the stopper is inserted. The end of this chain is heated in the flame of a lamp, and the stopper tightly fixed in its place. On allowing the hot chain to touch the phosphorus, it bursts into vivid combustion, filling the jar with thick white fumes, and covering its sides, for a few moments, with white flakes of phosphoric anhydride. At the commencement of the experiment, the water in the jar will be depressed, in consequence of the expansion of the air due to the heat produced in the burning of the phosphorus, but presently, when the combustion begins to decline, the water again rises, and continues to do so until it has ascended to the line (C), so as to occupy the place of one-fifth of the air employed in the experiment. The phosphorus will then have ceased to burn, the white flakes upon the sides of the jar will have acquired the appearance of drops of moisture, and the fumes will have gradually disappeared, until, in the course of half an hour, the air remaining in the jar will be as clear and transparent as before, the whole of the phosphoric anhydride having been absorbed by the water. The jar should now be sunk in water, so that the latter may attain to the same level without as within the jar. On removing the stopper, it will be found that the nitrogen in the jar will no longer support the combustion of a taper.

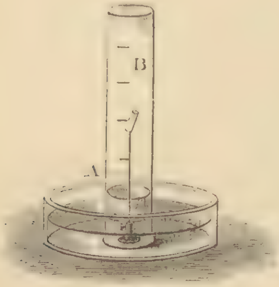

Fig. 50.

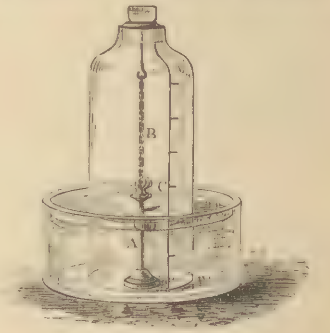

Fig. 51.

In the rigidly accurate determination of the relative proportions of oxygen and nitrogen in the air, it is of course necessary to guard against any error arising from the presence of the water, carbonic acid gas, and ammonia. With this view, Dumas and Boussingault, to whom we are originally indebted for our exact knowledge of the composition of the air, caused it to pass through a series of tubes (A, fig. 52) containing potash, in order to remove the carbonic acid gas, then through a second series (B) containing sulphuric acid, to absorb the ammonia and water; the purified air then passed through a glass tube (C) filled with bright copper heated to redness in a charcoal furnace, which removed the whole of the oxygen, and the nitrogen passed into the large globe (N).

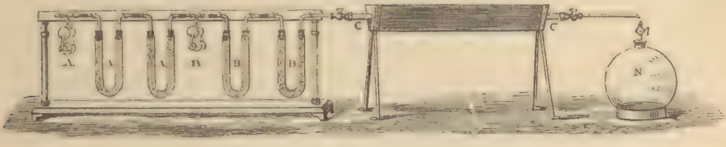

Fig. 52.—Exact analysis of air.

Both the tube (containing the copper) and the globe were carefully exhausted of air and accurately weighed before the experiment; on connecting the globe and the tube with the purifying apparatus, and slowly opening the stop-cocks, the pressure of the external air caused it to flow through the series of tubes into the globe destined to receive the nitrogen. When a considerable quantity of air had passed in, the stop-cocks were again closed, and after cooling, the weight of the globe was accurately determined. The difference between this weight and that of the empty globe, before the experiment, gave the weight of the nitrogen which had entered the globe; but this did not represent the whole of the nitrogen contained in the analysed air, for the tube containing the copper had, of course, remained full of nitrogen at the close of the experiment. This tube, having been weighed, was attached to the air-pump, the nitrogen exhausted from it, and the tube again weighed; the difference between the two weighings furnished the weight of the nitrogen remaining in the tube, and was added to the weight of that received in the globe. The oxygen was represented by the increase of the weight of the exhausted tube containing the copper, which was partially converted into oxide of copper, by combining with the oxygen of the air passed through it.

100 parts by weight of the air purified from water, carbonic acid gas, and ammonia, contain 77 parts of nitrogen and 23 parts of oxygen.

51. The nitrogen remaining after the removal of the oxygen from air in the above experiments was so called on account of its presence in nitre (saltpetre KNO_3). In physical properties it resembles oxygen, but is somewhat lighter than that gas, its specific gravity being 0.9713.

This difference in the specific gravities of the two gases is well exhibited by the arrangement shown in fig. 53. A jar of oxygen (O) is closed with a glass plate, and placed upon the table. A jar of nitrogen (N), also closed with a glass plate, is placed over it, so that the two gases may come in contact when the glass plates are removed. The nitrogen will float for some seconds above the oxygen, and if a lighted taper be quickly introduced through the neck of the upper jar, it will be extinguished in passing through the nitrogen, and will be rekindled brilliantly when it reaches the oxygen in the lower jar.

It might at first sight appear surprising that oxygen and nitrogen, though of different specific gravities, should exist in uniform proportions in all parts of the atmosphere, unless in a state of chemical combination: but an acquaintance with the property of diffusion (see 13) possessed by gases, teaches us that *gases will mix with each other in opposition to gravitation, and when mixed will always remain so.*

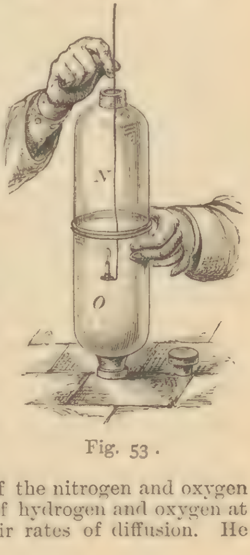

Fig. 53.

It was shown by Graham that a partial separation of the nitrogen and oxygen in air may be effected, on the same principle as that of hydrogen and oxygen at page 22, by taking advantage of the difference in their rates of diffusion. He devised, however, a more convenient process, founded upon the *dialytic* passage of the gases through caoutchouc, which he ascribed to the absorption of the gas by the solid material upon one side, and its escape on the other.

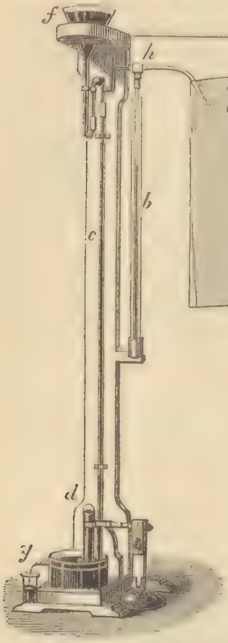

Fig. 54.—Sprengel's pump.
Dialysis of air.

A bag (*a*, fig. 54) is made of a fabric composed of a layer of caoutchouc between two layers of silk, such as that employed for waterproof garments; a piece of carpet is placed inside the bag to keep the sides apart, and the edges of the bag are made perfectly air-tight with solution of caoutchouc. To maintain a vacuum within the bag, it is supported by a rod *v*, and attached to *Sprengel's air-pump*, in which a stream of mercury, allowed to flow from a funnel (*f*) down a tube (*c*) six feet long, draws the air out of the bag, through a lateral tube (*h*), until all the air is exhausted, which is indicated by the barometer tube *b*, the lower end of which dips into a cistern of mercury. When the mercury in this tube stands at almost exactly the same height as the standard barometer, the exhaustion is complete. If a test-tube (*d*) filled with mercury be now inverted over the end of the long tube *c*, which is bent upwards for that purpose, the bubbles of air which are drawn through the sides of the vacuous bag, and carried down the long tube by the little pistons of liquid mercury as they fall, will pass up into the test-tube; when the latter is filled with the gas, its mouth is closed with the thumb, withdrawn from the mercury, and a match with a spark at the end inserted, when the spark will burst out into flame, showing that the specimen of air collected is much richer in oxygen than ordinary atmospheric air. The overflow tube *g* delivers the mercury which is to be returned to the funnel *f*.

The dialytic passage of oxygen through caoutchouc into a vacuum is twice as rapid as that of nitrogen, so that the air collected in the tube contains twice as much oxygen as the external air.

This dialytic passage of gases through solids is quite unconnected with the diffusibility of the gases, and appears to depend rather upon the chemical nature of the gas and of the solid. It is thus connected with the *occlusion* of gases by solids. It is in consequence of this dialytic passage that tubes of iron or platinum, which are quite impermeable by hydrogen at the ordinary temperature, will allow it to pass rapidly through their walls at high temperatures.

That air is simply a mechanical mixture of its component gases is amply proved by the circumstance that it possesses all the properties which would be predicted for a *mixture* of these gases in such proportions; whilst the essential feature of a *chemical compound* is, that its properties cannot be foreseen from those of its constituents.

The absence of active chemical properties is a very striking feature of nitrogen, and admirably adapts it for its function of diluting the oxygen in the atmosphere.

The chemical relations of air to animals and plants will be more appropriately discussed hereafter. (See *Carbonic Acid*, *Ammonia*.)

In considering the composition of air, much attention has been directed of late years to the *dust* or minute particles of solid matter which, although much heavier than air, are suspended in it by the action of currents, and may always be detected by a beam from the sun or the electric lamp or the lime-light, which would be invisible along its track through *optically pure* air.

The fine particles of mineral substances present in the dust are the probable cause of the crystallisation of super-saturated solutions of salts (p. 43) when exposed to air. The vegetable particles appear to contain minute seeds which germinate when deposited in certain liquid or moist solid substances, and give rise to *mould*, *mildew*, and fermentation. The animal particles are believed to contain the germs by the agency of which certain forms of disease are spread.

A sample of dust from one of the towers of Notre Dame which had not been entered for several years, contained one-third of organic matter rich in carbon, one-third of sand, one-sixth of chalk, and one-tenth of alkaline salts.

CARBON.

C = 12 parts by weight.*

52. This element is especially remarkable for its uniform presence in organic substances. The ordinary laboratory test by which the chemist decides whether a substance under examination is of organic origin, consists in heating it with limited access of air, and observing whether any blackening from separation of carbon (*carbonisation*) ensues.

Few elements are capable of assuming so many different aspects as carbon. It is met with transparent and colourless in the *diamond*, opaque, black, and quasi-metallic in *graphite* or black lead, dull and porous in wood *charcoal*, and under new conditions in *anthracite*, *coke*, and *gas-carbon*.

In nature, free carbon may be said to occur in the forms of diamond, graphite, and anthracite (the other varieties of coal containing considerable proportions of other elements).

Apart from its great beauty and rarity, the diamond possesses a special interest in chemical eyes, from its having perplexed philosophers up to the middle of the last century, notwithstanding the simplicity of the experiments required to demonstrate its true nature. The first idea of it appears to have been obtained by Newton, when he perceived its great power of refracting light, and thence inferred that, like other bodies possessing that property in a high degree, it would prove to be combustible ("an unctuous substance coagulated"). When the prediction was verified, the burning of diamonds was exhibited as a marvellous experiment, but no accurate observations appear to have been made till 1772, when Lavoisier ascertained, by burning diamonds suspended in the focus of a burning-glass in a confined portion of oxygen, that they were entirely converted into carbonic acid gas. In more recent times this experiment has been repeated with the utmost precaution, and the diamond has been clearly demonstrated to consist of carbon in a crystallised state.

A still more important result of this experiment was the exact determination of the composition of carbon dioxide, without which it would not be possible to ascertain exactly the proportion of carbon in any of its numerous compounds, since it is always weighed in that form.

The most accurate experiments upon the synthesis of carbon dioxide have been conducted with the arrangement represented in fig. 55.

Within the porcelain tube A, which is heated to redness in a charcoal fire, was placed a little platinum tray, accurately weighed, and containing a weighed quantity of fragments of diamond. One end of the tube was connected with a gas-holder B, containing oxygen, which was thoroughly purified by passing through the tube C, containing potash (to absorb any carbonic acid gas and chlorine which it might contain), and dried by passing over pumice soaked with concentrated sulphuric acid in D and E. To the other end of the porcelain tube A, there was attached a glass tube F, also heated in a furnace, and containing oxide of copper to convert into carbonic acid gas any carbonic oxide which might have been formed in the combustion of the diamond. The carbonic acid gas was then passed over pumice soaked with sulphuric acid in G, to remove any traces of moisture, and afterwards into a weighed bulb-apparatus H, containing solution of potash, and two weighed tubes I, K, containing, respectively, solid potash and sulphuric acid on pumice, to guard against the escape of aqueous vapour taken up by the excess of oxygen in its passage through the bulbs H. The increase of weight in H, I, K, represented the carbonic acid gas formed in the combustion of an amount of diamond indicated by the loss of weight suffered by the platinum tray, and the difference between the diamond consumed and the carbonic acid gas formed would express the amount of oxygen which had combined with the carbon. A large number of experiments conducted in this manner, both with diamond and graphite, showed that 12 parts of carbon furnished 44 parts of carbonic acid gas, and consumed, therefore, 32 parts of oxygen.

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* The volume occupied by carbon in the form of vapour is not known by direct experiment, its vapour never having been obtained in a measurable form.

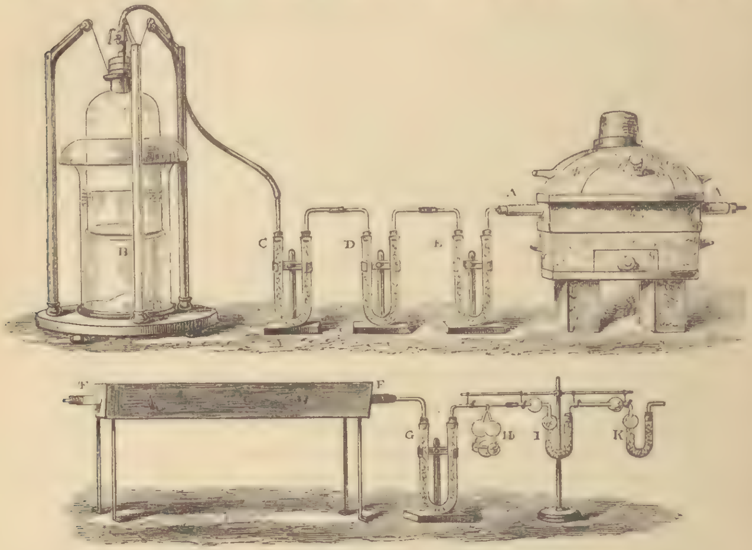

Fig. 55.—Exact synthesis of carbonic acid gas.

A convenient arrangement for burning a diamond in oxygen is shown in fig. 56. The diamond is supported in a short helix of platinum wire A, which is attached to the copper wires B B, passing through the cork C, and connected with the terminal wires of a Grove's battery of five or six cells. The globe having been filled with oxygen by passing the gas down into it till a match indicates that the excess of oxygen is streaming out of the globe, the cork is inserted, and the wires connected with the battery. When the heat developed in the platinum coil, by the passage of the current, has raised the diamond to a full red heat, the connexion with the battery may be interrupted, and the diamond will continue to burn with steady and intense brilliancy.

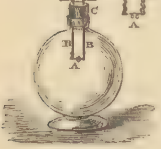

Fig. 56.

To an observer unacquainted with the satisfactory nature of this demonstration, it would appear incredible that the transparent diamond, so resplendent as to have been reputed to emit light, should be identical in its chemical composition with graphite (*plumbago* or *black lead*), from which, in external appearance, it differs so widely. For this difference is not confined to their colour; in crystalline form they are not in the least alike, the diamond occurring generally in octahedral crystals, while graphite is found either in *amorphous* masses (that is, having no definite crystalline form), or in six-sided plates which are not geometrically allied with the form assumed by the diamond. Carbon, therefore, is *dimorphous*, or occurs in two distinct crystalline forms. Even in weight, diamond and graphite are very dissimilar, the former having an average specific gravity of 3.5 and the latter of 2.3. Again, a crystal of diamond is the hardest of all substances, whence it is used for cutting and for writing upon glass, but a mass of graphite is soft and easily cut with a knife. The diamond is a non-conductor of electricity, but the conducting power of graphite renders it useful in the electrotype process.

Diamonds are chiefly obtained from Golconda, Borneo, and the Brazils. They usually occur in sandstone rock or in mica slate. The hardness of the diamond renders it necessary to employ diamond-dust for the purpose of cutting and polishing it, which is effected with the aid of a revolving disk of steel, to the surface of which the diamond-dust is applied in the form of a paste made with oil. The crystal in its natural state is best fitted for the purpose of the glazier, for its edges are usually somewhat curved, and the angle formed by these cuts the glass deeply, while the angle formed by straight edges, like those of an ordinary jeweller's diamond, is only adapted for scratching or writing upon glass. Drills with diamond points have been employed in tunnelling through hard rocks. The diamond-dust used for polishing, &c., is obtained from a dark amorphous diamond (*Carbonado*) found at Bahia in the Brazils; 1000 ounces annually are said to have been occasionally obtained from this source. When burnt, the diamond always leaves a minute proportion of ash of a yellowish colour in which silica and oxide of iron have been detected. A genuine diamond may be known by its combining the three qualities of extreme hardness, enabling it to scratch hardened steel, high specific gravity (3.52), and insolubility in hydrofluoric acid. Sapphire (Al_2O_3) is nearly as hard as diamond, but its specific gravity is about 4.

Although the diamond, when preserved from contact with the air, may be heated very strongly in a furnace, without suffering any change, it is not proof against the intense heat of the discharge taking place between two carbon points attached to the terminal wires of a powerful galvanic battery. If the experiment be performed in a vessel exhausted of air, the diamond becomes converted into a black coke-like mass which closely resembles graphite in its properties.

Graphite always leaves more ash than the diamond, consisting chiefly of the oxides of iron and manganese, with particles of quartz, and sometimes titanic dioxide. The purest specimens are those of compact amorphous graphite from Borrowdale in Cumberland; an inferior variety, imported from Ceylon, is crystalline, being composed of hexagonal plates. Graphite is obtained artificially in the manufacture of cast iron: in some cases, a portion of the carbon of the cast iron separates in cooling, in the form of crystalline scales of graphite, technically called *kish*. In the grey variety of cast iron these scales of graphite are diffused through the mass of the metal, and are left undissolved when the iron is dissolved by an acid.

Graphite is far more useful than the diamond, for, in addition to its application in black-lead pencils, and for covering the surface of iron in order to protect it from rust, it is largely employed, in admixture with clay, for the fabrication of the plumbago crucibles (*blue pots*), which are so valuable to the metallurgist for their power of resisting high temperatures and sudden change of temperature. Graphite is also sometimes employed for lubricating, to diminish friction in machinery, and for *facing* or imparting a glazed surface to gunpowder.

Inferior kinds of graphite are treated by *Brodie's* process. The graphite is heated with 2 parts of sulphuric acid and $\frac{1}{14}$th or $\frac{1}{20}$th of potassium chlorate. A part of the graphite is thus oxidised and converted into *graphitic acid*, $C_{11}H_4O_5$. When the graphite so treated is washed, dried, and heated to redness, the graphitic acid is decomposed, evolving steam and carbonic oxide gas, which swells up the graphite to a light voluminous powder which can be separated from the heavy earthy impurities by floating it in water. When much silica is present in the graphite, a little sodium fluoride is added after the potassium chlorate has been decomposed.

(Anthracite and the other varieties of coal will be described in a separate section.)

53. Several varieties of carbon, obtained by artificial processes, are employed in the arts. The most important of these are *lamp black*, *wood charcoal*, and *animal charcoal*.*

Lamp black approaches more nearly in composition to pure carbon than either of the others, and is the soot obtained from the imperfect combustion of resinous and tarry matters (or of highly bituminous coal), from which source it derives the small quantities of resin, nitrogen, and sulphur which it contains. The uses of this substance, as an ingredient of pigments, of printing-ink, and of blacking, depend evidently more upon its black colour than upon its chemical properties. *Diamond black* is a very pure variety of lamp black obtained by the imperfect combustion of the natural hydrocarbon gas of the Ohio petroleum region. *Spanish black* is charcoal made from waste cork.

Wood charcoal presents more features which arrest the attention of the chemist, as well on account of its specific properties, as of the influence exercised by the method adopted for obtaining it, upon its fitness for the particular purpose which it may be destined to serve.

If a piece of wood be heated in an ordinary fire, it is speedily consumed, with the exception of a grey ash consisting of the incombustible mineral substances which it contained; if the experiment were performed in such a manner that the products of combustion of the wood could be collected, these would be found to consist of carbonic acid gas and water; woody fibre is composed of carbon, hydrogen, and oxygen ($C_6H_{10}O_5$), and when it is burnt, the oxygen, in conjunction with more oxygen derived from the air, converts the carbon and hydrogen into carbon dioxide and water. But if the wood be heated in a glass tube, closed at one end, it will be found impossible to reduce it, as before, to an ash, for a mass of charcoal will remain, having the same form as that of the piece of wood; in this case, the oxygen of the air not having been allowed free access to the wood, no true combustion has taken place, but the wood has undergone *destructive distillation*, that is, its elements have arranged themselves, under the influence of the high temperature, into different forms of combination, for the most part simpler in their chemical composition than the wood itself, and capable, unlike the wood, of enduring that temperature without decomposition; thus, it is merely an exchange of an unstable for a stable equilibrium of the particles of matter composing the wood.

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* The term *pseudo-carbons* has been proposed for bodies of this description characterised by a high percentage of carbon, and, in many respects, simulating the element itself (Cross and Bevan, *Phil. Mag.*, May 1882).

(DEFINITION.—*Destructive distillation* is the resolution of a complex substance into simpler vapours and gases under the influence of heat, out of contact with air.)

The vapours issuing from the mouth of the tube will be found acid to blue litmus paper; they have a peculiar odour, and readily take fire on contact with flame. These will be more particularly noticed hereafter, as they contain some very useful substances. The charcoal which is left is not pure carbon, but contains considerable quantities of oxygen and hydrogen with a little nitrogen, and the mineral matter or ash of the wood.

When the charcoal is to be used for fuel, it is generally prepared by a process in which the heat developed by the combustion of a portion of the wood is made to effect the charring of the rest. With this view the billets of wood are built up into a heap (fig. 57) around stakes driven into the ground, a passage being left so that the heap may be kindled in the centre. This mound of wood, which is generally from 30 to 50 feet in diameter, is closely covered with turf and sand, except for a few inches around the base, where it is left uncovered to give vent to the vapour of water expelled from the wood in the first stage of the process. When the heap has been kindled in the centre, the passage left for this purpose is carefully closed up. After the combustion has proceeded for some time, and it is judged that the wood is perfectly dried, the open space at the base is also closed, and the heap left to smoulder for three or four weeks, when the wood is perfectly carbonised.

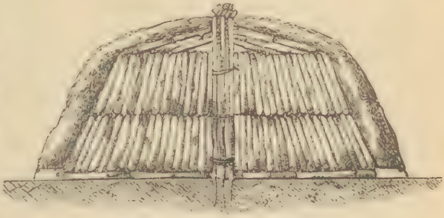

Fig. 57.—Charcoal heap.

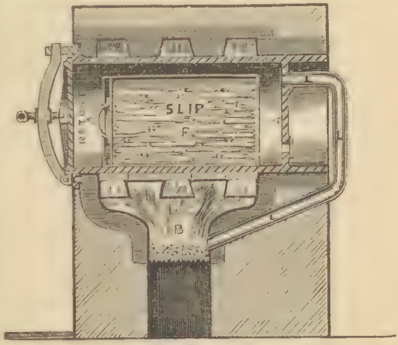

Fig. 58.—Charcoal retort.

Upon an average, 22 parts of charcoal are obtained by this process from 100 of wood.

A far more economical process for preparing charcoal from wood consists in heating it in a perforated iron case or *slip* (F, fig. 58) placed in an iron retort A, from which the gases and vapours are conducted by the pipe L into the furnace B, where they are consumed.

On the small scale, the operation may be conducted in a glass retort, as shown in fig. 59, where the water, tar, and naphtha are deposited in the globular receiver, and the inflammable gases are collected over water.

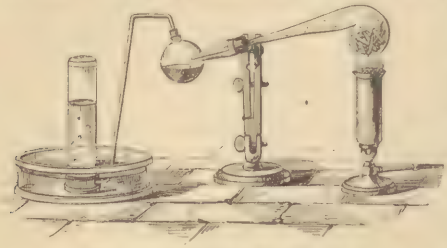

Fig. 59.—Distillation of wood.

The infusibility of the charcoal left by wood accounts for its very great porosity, upon which some of its most remarkable and useful properties depend. The application of charcoal for the purpose of "sweetening" fish and other food in a state of incipient putrefaction has long been practised, and more recently charcoal has been employed for *deodorising* all kinds of putrefying and offensive animal or vegetable matter. This property of charcoal depends upon its power of absorbing into its pores very considerable quantities of the gases, especially of those which are easily absorbed by water. Thus, 1 cubic inch of charcoal is capable of absorbing about 100 cubic inches of ammonia gas and 50 cubic inches of sulphuretted hydrogen, both which are conspicuous among the offensive results of putrefaction. This condensation of gases by charcoal is a mechanical effect, and does not involve a chemical combination of the charcoal with the gas; it is exhibited most powerfully by charcoal which has been recently heated to redness in a closed vessel, and cooled out of contact with air by plunging it under mercury. Eventually the offensive gases absorbed by the charcoal are chemically acted on by the oxygen of the air in its pores. A cubic inch of wood charcoal absorbs nearly 10 cubic inches of oxygen, and when the charcoal containing the gas thus condensed is presented to another gas which is capable of undergoing oxidation, this latter gas is oxidised and converted into inodorous products. Thus, if charcoal be exposed to the action of air containing sulphuretted hydrogen gas (H_2S), it condenses within its pores both this gas and the atmospheric oxygen, which slowly converts it into sulphuric acid (H_2SO_4).

The great porosity of wood charcoal is strikingly exhibited by attaching a piece of lead to a stick of charcoal (fig. 60), so as to sink it in a cylinder of water, which is then placed under the receiver of the air-pump. On exhausting the air, innumerable bubbles will start from the pores of the charcoal, causing brisk effervescence. If a glass tube 16 or 18 inches long be thoroughly filled with ammonia gas (fig. 61), supported in a trough containing mercury, and a small stick of recently calcined charcoal introduced through the mercury into the tube, the charcoal will absorb the ammonia so rapidly that the mercury will soon be forced up and fill the tube, carrying the charcoal up with it. On removing the charcoal, and placing it upon the hand, a sensation of cold will be perceived from the rapid escape of ammonia, perceptible by its odour.

By exposing a fragment of recently calcined wood charcoal under a jar filled with hydrosulphuric acid gas for a few minutes, so that it may become saturated with the gas, and then covering it with a jar of oxygen, the latter gas will act upon the former with such energy that the charcoal will burst into vivid combustion. The jar must not be closed air-tight at the bottom, or the sudden expansion may burst it. Charcoal in powder exposed in a porcelain crucible may also be employed in the same way. It should be pretty strongly heated in the covered crucible, and allowed to become nearly cool before being exposed to the hydrosulphuric acid.

Charcoal prepared from hard woods absorbs the largest volume of gas. Thus logwood charcoal has been found to absorb 111 times its volume of the ammoniacal gas. Charcoal made from the shell of the cocoa-nut is even more absorbent, although its pores are quite invisible, and its fracture exhibits a semimetallic lustre.

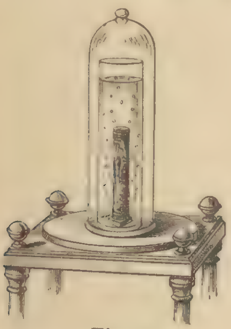

Fig. 60.

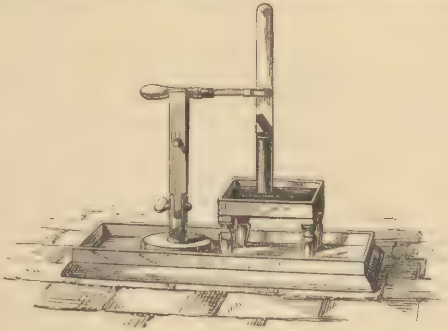

Fig. 61.

As the gases which are evolved in putrefaction are of a poisonous character, the power of wood charcoal to remove them acquires great practical importance, and is applied in very many cases; the charcoal in coarse powder is thickly strewn over matters from which the effluvium proceeds, or is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, &c. It has even been placed in a flat box of wire gauze to be fixed as a ventilator before a window through which the contaminated air might have access, and respirators constructed on the same principle have been found to afford protection against poisonous gases and vapours. The ventilating openings of sewers in the streets may also be fitted with cases containing charcoal for the same purpose. Water is often filtered through charcoal in order to free it from the noxious and putrescent organic matters which it sometimes contains. For all such uses the charcoal should have been recently heated to redness in a covered vessel, in order to expel the moisture which it attracts when exposed to the air; and the charcoal which has lost its power of absorption will be found to regain it in great measure when heated to redness.

This power of absorption which charcoal possesses is not confined to gases, for many liquid and solid substances are capable of being removed by that agent from their solution in water. This is most readily traced in the case of substances which impart a colour to the solution, such colour being often removed by the charcoal; if port wine or infusion of logwood be shaken with powdered charcoal (especially if the latter has been recently heated

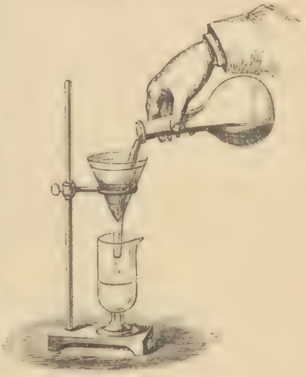

Fig. 62.—Filtration.

to redness in a closed crucible), the liquid, when filtered through blotting-paper (fig. 62), will be found to have lost its colour; the colouring matter, however, seems merely to have adhered to the charcoal, for it may be extracted from the latter by treatment with a weak alkaline liquid.

The *decolorising power* of wood charcoal is very feeble in comparison with that possessed by *bone-black* or *animal charcoal*, which is obtained by heating bones in vessels from which the air is excluded. Bones are composed of about one-third of animal and two-thirds of mineral substances, the latter including calcium phosphate, which amounts to more than half the weight of the bone, and a little calcium carbonate. When bone is heated, as in a retort, so that air is not allowed to have free access to it, the animal matter undergoes destructive distillation, its elements—carbon, hydrogen, nitrogen, and oxygen—assuming other forms, the greater part of the three last elements, together with a portion of the carbon, escaping in different gaseous and vaporous products, while a considerable proportion of the carbon remains behind. intimately mixed with the earthy ingredients of the bone, and constituting the substance known as animal charcoal. The great difference between the products of the destructive distillation of bone and of wood deserves a passing notice. If a fragment of bone or a shaving of horn be heated in a glass tube closed at one end, the vapours which are evolved will be found strongly *alkaline* to test-papers, while those furnished by the wood were *acid;* this difference is to be ascribed mainly to the presence of nitrogen in the bone, wood being nearly free from that element; it will be found to hold good, as a general rule. that the results of the destructive distillation of animal and vegetable matters containing much nitrogen are alkaline, from the presence of ammonia (NH_3) and similar compounds, while those furnished by non-nitrogenised substances possess acid characters: the peculiar odour which is emitted by the heated bone is characteristic, and affords us a test by which to distinguish roughly between nitrogenised and non-nitrogenised bodies.

An examination of the charred mass remaining as the ultimate result of the action of heat upon bone, shows it to contain much less carbon than that furnished by wood, for the bone charcoal contains nearly nine-tenths of its weight of phosphate (with a little carbonate) of calcium: the consequence of the presence of so large an amount of earthy matter must be to extend the particles of carbon over a larger space, and thus to expose a greater surface for the adhesion of colouring matters, &c. This may partly help to explain the very great superiority of bone-black to wood charcoal as a decolorising agent, and the explanation derives support from the circumstance, that when animal charcoal is deprived of its earthy matter, for chemical uses, by washing with hydrochloric acid, its decolorizing power is very considerably reduced. The application of this variety of charcoal is not confined to the chemical laboratory, but extends to manufacturing processes. The sugar refiner decolorises his syrup by filtering it through a layer of animal charcoal, and the distiller employs charcoal to remove the fousel oil with which distilled spirits are frequently contaminated.

Carbon is remarkable, among elementary bodies, for its indisposition to enter directly into combination with the other elements, whence it follows that most of the compounds of carbon have to be obtained by indirect processes. This element appears, indeed, to be incapable of uniting with any other at the ordinary temperature, and this circumstance is occasionally turned to useful account, as when the ends of wooden stakes are charred before being plunged into the earth, when the action of the atmospheric oxygen, which, in the presence of moisture, would be very active in effecting the decay of the wood, is resisted by the charcoal into which the external layer has been converted. The employment of black-lead to protect metallic surfaces from rust is another application of the same principle. At a high temperature, however, carbon combines readily with oxygen, sulphur, and with some of the metals, and, at a very high temperature, even with hydrogen and nitrogen. The tendency of carbon to combine with oxygen under the influence of heat, is shown when a piece of charcoal is strongly heated at one point, when the carbon at this point at once combines with the oxygen of the surrounding air (forming carbonic acid gas), and the heat developed by this combustion raises the neighbouring particles of carbon to the temperature at which the element unites with oxygen, and thus the combustion is gradually propagated throughout the mass, which is ultimately converted entirely into carbonic acid gas, nothing remaining but the white ash, composed of the mineral substances derived from the wood employed for preparing the charcoal. It is worthy of remark, that if charcoal had been a better conductor of heat, it would not have been so easily kindled, since the heat applied to any point of the mass would have been rapidly diffused over its whole bulk, and this point could not have attained the high temperature requisite for its ignition, until the whole mass had been heated nearly to the same degree; this is actually found to be the case in charcoal which has been very strongly heated (out of contact with air), when its conducting power is greatly improved, and it kindles with very great difficulty. The *calorific value* of carbon in the form of wood charcoal is represented by the number 8080, that is, 1 gr. of carbon, when burnt so as to form carbonic acid gas, is capable of raising 8080 grs. of water from 0° C. to 1° C.

A given weight of charcoal will produce twice as much available heat as an equal weight of wood, since the former contains more actual fuel and less oxygen, and much of the heat evolved by the wood is absorbed or rendered latent in the steam and other vapours which are produced by the action of heat upon it. The attraction possessed by carbon for oxygen at a high temperature is turned to account in metallurgic operations, when coal and charcoal are employed for extracting the metals from their compounds with oxygen.*

The unchangeable solidity of carbon is another remarkable feature. It is stated that some approach has been made, at extremely high temperatures, to the fusion and vaporisation of carbon, but it cannot be said to have been fairly established that this element is able to exist in any other than the solid form. Nor can any substance be found by the aid of which carbon may be brought into the liquid form by the process of solution; for although charcoal gradually disappears when boiled with sulphuric and nitric acids, it does not undergo a simple solution, but is converted, as will be seen hereafter, into carbon dioxide.

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* Easily reducible oxides, such as oxide of lead, give carbon dioxide when heated with charcoal; $2PbO + C = Pb_2 + CO_2$, but oxides which are not easily reducible, such as oxide of zinc, give carbonic oxide; $ZnO + C = CO + Zn$.

The very striking difference in properties exhibited by diamond, graphite, and charcoal, lead to the belief that they consist of dissimilar carbon molecules. The investigation of the specific heats of these three varieties affords some grounds for the belief that the diamond molecule consists of four atoms, the graphite molecule of three atoms, and the charcoal molecule of two atoms of carbon.

When an element is capable of appearing in two or more forms, having different physical properties, these forms are said to be *allotropic*.

(DEFINITION.—*Allotropy* is the assumption of different properties without loss of chemical identity.)

Such cases, like those of *isomerism* among the compounds of carbon (see *Organic Chemistry*), will probably be explained by differences in the position and arrangement of the atoms in the molecule.

Pure carbon is prepared with some difficulty; the charcoal obtained by heating some pure organic substance containing C, H, and O, such as white sugar-candy, in a closed crucible, is heated in a porcelain tube, as strongly as possible, in a current of dry chlorine gas until no more HCl is produced. The residue in the tube is nearly pure carbon.

54. COAL.—The various substances which are classed together under the name of coal are characterised by the presence of carbon as a largely predominant constituent, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain mineral matters which compose the ash. Coal appears to have been formed by a peculiar decomposition or fermentation of buried vegetable matter, resulting in the separation of a large proportion of its hydrogen in the form of marsh-gas (CH_4), and similar compounds, and of its oxygen in the form of carbonic acid gas (CO_2), the carbon accumulating in the residue. Thus, cellulose ($C_6H_{10}O_5$), which constitutes the bulk of woody fibre, might be imagined to decompose according to the equation $2C_6H_{10}O_5 = 5CH_4 + 5CO_2 + C_2$, and the occurrence of marsh-gas, and of the paraffin hydrocarbons of similar composition, as well as of carbonic acid gas, in connexion with deposits of coal, supports this account of its formation. Marsh-gas and carbonic acid gas are the ordinary products of the fermentation of vegetable matter, and a spontaneous carbonisation is often witnessed in the "heating" of damp hay. But just as the action of heat upon wood produces a charcoal containing small quantities of the other organic elements, so the carbonising process by which the plants have been transformed into coal has left behind some of the hydrogen, oxygen, and nitrogen; the last, as well probably as a little of the sulphur, having been derived from the vegetable albumen and similar substances which are always present in plants. The chief part of the sulphur is generally present in the form of iron pyrites (FeS_2), derived from some extraneous source. The examination of a peat-bog is very instructive with reference to the formation of coal, as affording examples of vegetable matter in every stage of decomposition, from that in which the organised structure is still clearly visible, to the black carbonaceous mass which only requires consolidation by pressure in order to resemble a true coal. In some cases an important part in the formation of coal may have been played by slow oxidation or decay of the vegetable matter at the expense of atmospheric oxygen held in solution by water;

since the hydrogen of the compound would be removed by oxidation taking place at a low temperature, giving rise to a gradual increase in the percentage of carbon.

The three principal varieties of coal—*lignite*, *bituminous coal*, and *anthracite*—present us with the material in different stages of carbonisation; the lignite, or brown coal, presenting indications of organised structure, and containing considerable proportions of hydrogen and oxygen, while anthracite often contains little else than carbon and the mineral matter or ash. The following table shows the progressive diminution in the proportions of hydrogen and oxygen in the passage from wood to anthracite :—

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12.18	83.07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal . . .	100	6.12	21.23
Anthracite	100	2.84	1.74

The combustion of coal is a somewhat complex process, in consequence of the re-arrangement which its elements undergo when the coal is subjected to the action of heat.

As soon as a flame is applied to kindle the coal, the heated portion undergoes destructive distillation, evolving various combustible gases and vapours, which take fire and convey the heat to remoter portions of the coal. Whilst the elements of the exterior portion of coal are undergoing combustion, the heat thus evolved is submitting the interior of the mass to destructive distillation, resulting in the production of various compounds of carbon and hydrogen. Some of these products, such as marsh-gas (CH_4) and olefiant gas (C_2H_4), burn without smoke, while others, like benzene (C_6H_6) and naphthalene ($C_{10}H_8$), which contain a very large proportion of carbon, undergo partial combustion, and a considerable quantity of carbon, not meeting with enough heated oxygen in the vicinity to burn it entirely, escapes in a very finely divided state as smoke or soot, which is deposited in the chimney, mixed with a little ammonium carbonate and small quantities of other products of the distillation of coal. When the gas has been expelled from the coal, there remains a mass of coke or cinder, which burns with a steady glow until the whole of its carbon is consumed, and leaves an *ash*, consisting of the mineral substances present in the coal. The final results of the perfect combustion of coal would be carbonic acid gas (CO_2), water (H_2O), nitrogen, a little sulphurous acid gas (SO_2), and ash. The production of smoke in a furnace supplied with coal may be prevented by charging the coal in small quantities at a time in front of the fire, so that the highly carbonaceous vapours must come in contact with a large volume of heated air before reaching the chimney. In arrangements for consuming the smoke, hot air is judiciously admitted at the back of the fire, in order to meet and consume the heated carbonaceous particles before they pass into the chimney.

The difference in the composition of the several varieties of coal gives rise to a great difference in their mode of burning.

The following table exhibits the composition of representative specimens of the four principal varieties :—

Composition of Coal.

	Lignite.	Bituminous Coal.	Wigan Cannel.	Anthracite.
Carbon	66.32	78.57	80.06	90.39
Hydrogen	5.63	5.29	5.53	3.28
Nitrogen	0.56	1.84	2.12	0.83
Oxygen	22.86	12.88	8.09	2.98
Sulphur	2.36	0.39	1.50	0.91
Ash *	2.27	1.03	2.70	1.61
	100.00	100.00	100.00	100.00

The lignites furnish a much larger quantity of gas under the action of heat (and therefore burn with more flame than the other varieties), leaving a coke which retains the form of the original coal; while bituminous coal softens and cakes together,—a useful property, since it allows even the dust of such coal to be burnt, if the fire be judiciously managed. Anthracite (*stone coal* or *Welsh coal*) is much less easily combustible than either of the others, and, since it yields but little gas when heated, it usually burns with little flame or smoke. This variety of coal is so compact that it will not usually burn in ordinary grates, but is much employed for furnaces. (See *Chemistry of Fuel.*)

Jet resembles cannel coal in composition.

Accidents occasionally arise from the spontaneous combustion of coal, especially when shipped in a damp state. This appears to be due, in some cases, to the development of heat by the action of atmospheric oxygen on the iron pyrites or *coal-brasses* contained in the coal. Sometimes the coal itself may be capable of slow combination with oxygen, and unless due provision be made for the escape of the heat, its accumulation may raise the temperature to a dangerous degree.

55. Carbon is capable of combining with oxygen in two proportions, forming the compounds known as *carbonic oxide* or *carbon monoxide* (CO) and *carbon dioxide* (CO_2).

CARBON DIOXIDE OR CARBONIC ACID GAS.

CO_2=44 parts by weight=2 vols. 44 grammes=22.32 litres.

56. It has been already mentioned that carbonic acid gas is a component of the atmosphere, which usually contains about 3.5 volumes of carbonic acid gas in 10000 volumes of air. The proportion is less at high altitudes. Thus, at 395 metres above sea-level, the air contained 3.13 vols. in 10000; at 1446 metres, 2.03 vols.; and at 1884 metres, 1.72 vol. It is greater during the night than in the day, since plants only decompose carbon dioxide in daylight, and actually exhale it during the night. The oleander leaf was found to decompose, on an average, in sunlight, 1108 cubic centimetres (67.6 cubic inches) of CO_2 per square metre (about 11 square feet) of leaf-surface, per hour; but, in the dark, the same surface emitted 70 c.c. (4.27 cub. in.) of CO_2 per hour. Flowers, even in daylight, absorb oxygen and evolve CO_2.

The proportion of CO_2 does not vary materially in the neighbourhood of a town.

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* The ash of coal consists chiefly of silica, alumina, and peroxide of iron. When lime is present in the ash, it is liable to fuse into a rough glass or *clinker* which adheres to the grate-bars and causes much inconvenience.

Carbonic acid gas is chiefly formed by the operation of the atmospheric oxygen in supporting combustion and respiration. All substances used as fuel contain a large proportion of carbon, which, in the act of combustion, combines with the oxygen, and escapes into the atmosphere in the form of carbonic acid gas. In the process of respiration, the carbonic acid gas is formed from the carbon contained in the different portions of the animal frame to which oxygen is conveyed by the blood; the latter, in passing through the lungs, gives out, in exchange for the oxygen, a quantity of carbonic acid gas produced by the union of a former supply of oxygen with the carbon of the different organs to which the blood is supplied, which, as they are constantly corroded and destroyed by this oxidising action of the blood, are repaired by the supply of food taken into the body. This conversion of carbon of the organs into carbonic acid gas will be again referred to; it will be at once evident that it must be concerned in the maintenance of the animal heat.

The leaves of plants, under the influence of light, have the power of decomposing the carbonic acid gas of the atmosphere, the carbon of which is applied to the production of vegetable compounds forming portions of the organism of the plant, and when this dies, the carbon is restored, after a lapse of time more or less considerable, to the atmosphere, in the same form, namely, that of carbonic acid gas, in which it originally existed there. If a plant should have been consumed as food by animals, its carbon will have been eventually converted into carbonic acid gas by respiration; the use of the plant as fuel, either soon after its death (wood), or after the lapse of time has converted it into coal, will also consign its carbon to the air in the form of carbonic acid gas. Even if the plant be left to *decay*, this process involves a slow conversion of its carbon into carbonic acid gas by the oxygen of the air.

Putrefaction and fermentation are also very important processes concerned in restoring to the air, in the form of carbonic acid gas, the carbon contained in dead vegetable and animal matter. Although, in a popular sense, these two processes are distinct, yet their chemical operation is of the same kind, consisting in *the resolution of a complex substance into simpler forms, produced by contact with some minute living plant or animal.* The discussion of the true nature of the process (which is even now somewhat obscure) would be premature at this stage, and it will suffice for the present to state that carbonic acid gas is one of the simpler forms into which the carbon is converted by the metamorphosis which ensues so quickly upon the death of animals and vegetables.

The production of carbonic acid gas in combustion, respiration, and fermentation, may be very easily proved by experiment. If a dry bottle be placed over a burning wax taper standing on the table, the sides of the bottle will be covered with dew from the combustion of the hydrogen in the wax; and if a little clear lime-water be shaken in the bottle, the milky deposit of calcium carbonate will indicate the formation of the carbonic acid gas.

By arranging two bottles, as represented in fig. 63, and inspiring through the tube A, air will bubble through the lime-water in B, before entering the lungs, and will then be found to contain too little carbonic acid gas to produce a milkiness, but on expiring the air, it will bubble through C, and will render the lime-water in this bottle very distinctly turbid.

If a little sugar be dissolved in eight or ten times its weight of warm (not hot) water, in the flask A (fig. 64), and a little dried yeast, previously rubbed down with water, added, fermentation will commence in the course of an hour or less, and carbonic acid gas may be collected in the jar B.

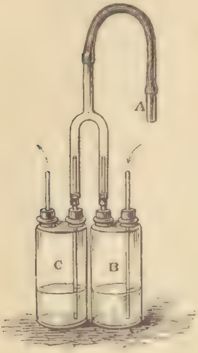

Fig. 63.

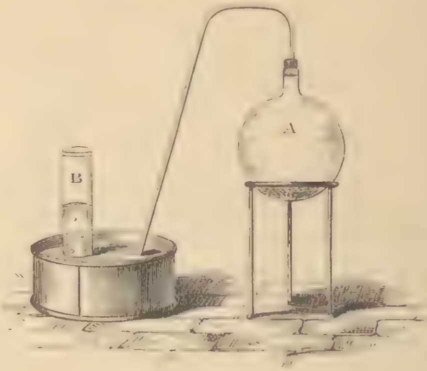

Fig. 64.

57. In the mineral kingdom, carbon dioxide is pretty abundant. The gas issues from the earth in some places in considerable quantity, as at Nauheim, where there is said to be a spring exhaling about 1,000,000 lbs. of the gas annually. Many spring waters, those of Seltzer and Pyrmont, for example, are very highly charged with the gas.

Carbonic acid gas is found in the air of soils in larger proportion than in the atmosphere, sometimes amounting to 16 vols. in 10,000. It increases with the temperature, and appears to originate from some of the lowest forms of animal life.

But it occurs in far larger quantity in the immense deposits of *limestone*, marble, and chalk, which compose so large a portion of the crust of the globe. Calcium carbonate is also met with in the animal kingdom. Oyster-shells contain 98 per cent. and egg-shells 97 per cent. of it, and pearls contain about two-thirds of their weight.

The expulsion of the carbonic acid gas from limestone ($CaCO_3$) forms the object of the process of *lime burning*, by which the large supply of lime (CaO) is obtained for building and other purposes. But if it be required to obtain the carbonic acid gas without regard to the lime, it is better to decompose the carbonate with an acid.

Preparation of carbonic acid gas.—The form of the calcium carbonate, and the nature of the acid employed, are by no means matters of indifference. If dilute sulphuric acid be poured upon fragments of marble, the effervescence which occurs at first soon ceases, for the surface of the marble becomes coated with the nearly insoluble calcium sulphate, by which it is protected from the further action of the acid—

$$\underset{\text{Marble.}}{CaCO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate}\\\text{of lime.}}}{CaSO_4} + H_2O + CO_2;$$

if the marble be finely powdered, or if powdered chalk be employed, each particle of the carbonate will be acted upon. When lumps of calcium carbonate are acted upon by hydrochloric acid, there is no danger that any will escape the action of the acid, for the calcium chloride produced is one of the most soluble salts—

$$\underset{\text{Marble.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + CO_2.$$

For the ordinary purposes of experiment, carbonic acid gas is most easily obtained by the action of diluted hydrochloric acid upon small fragments of marble (fig. 65), the latter being covered with water, and hydrochloric acid poured in through the funnel-tube. The gas may be collected by downward displacement.

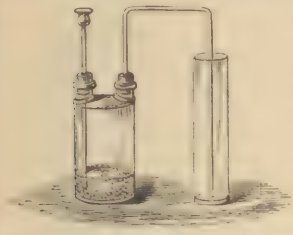

Fig. 65.—Preparation of carbonic acid gas.

58. *Properties of carbon dioxide.*—Carbonic acid gas is invisible, like the gases already examined, but is distinguished by a peculiar pungent odour, as is perceived in soda-water. It is more than half as heavy again as atmospheric air, its specific gravity being 1.529, which causes its accumulation near the floor of such confined spaces as the Grotto del Cane, where it issues from fissures in the rock.

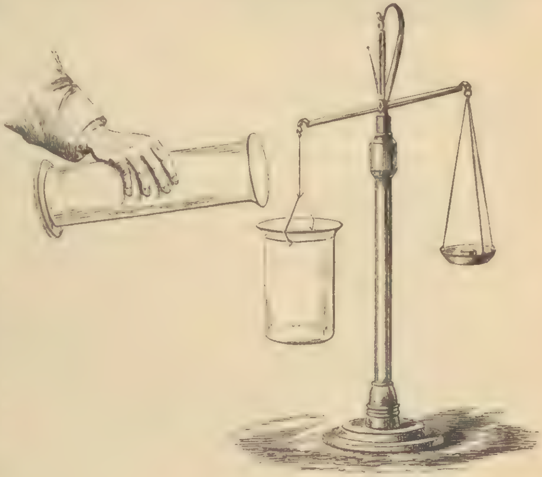

Fig. 66.

The high specific gravity of carbonic acid gas may be shown by pouring it into a light jar attached to a balance, and counterpoised by a weight in the opposite scale (fig. 66.)

Another favourite illustration consists in floating a soap-bubble on the surface of a layer of the gas generated in the large jar (fig. 67), by pouring diluted sulphuric acid upon a few ounces of chalk made into a thin cream with water.

If a small balloon, made of collodion, be placed in the jar A (fig. 68), it will ascend on the admission of carbonic acid gas through the tube B.

If smouldering brown paper be held at the mouth of a jar, like that in fig. 68, the smoke will float upon the surface of the carbonic acid gas, and will sink with it on removing the stopper.

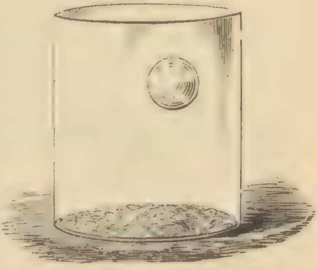

Fig. 67.

The power which carbonic acid gas possesses of extinguishing flame is very important, and has received practical application in the case of burning mines which must otherwise have been flooded with water.* Many attempts have also been made from time to time to employ this gas for subduing ordinary conflagrations, but their success has hitherto been very partial. It will be remembered that pure nitrogen is also capable of extinguishing the flame of a taper, but a large proportion of this gas may be present in air without affecting the flame, whereas a taper is extinguished in air containing one-eighth of its volume of carbonic acid gas, and is sensibly diminished in brilliancy by a much smaller proportion of the gas.

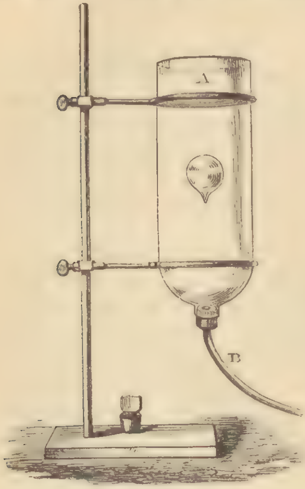

Fig. 68.

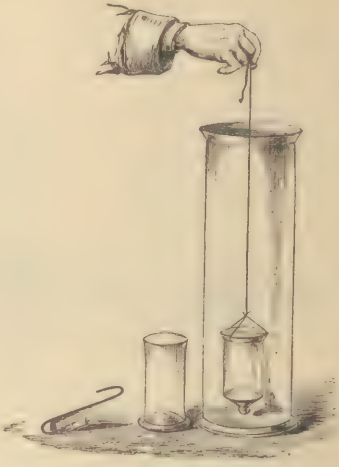

Fig. 69.

The power of extinguishing flame, conjoined with the high density of carbonic acid gas, admits of some very interesting illustrations.

Carbonic acid gas may be poured from some distance upon a candle, and will extinguish it at once. By employing a gutter, made of thin wood or stiff paper, to conduct the gas to the flame, it may be extinguished from a distance of several feet.

A large torch of blazing tow may be plunged beneath the surface of the carbonic acid gas in the jar (fig. 67).

Carbonic acid gas may be raised in a glass bucket (fig. 69) from a large jar, and poured into another jar, the air in which has been previously tested with a taper.

A wire stand with several tapers fixed at different levels may be placed in the jar A (fig. 70), and carbonic acid gas gradually admitted through a flexible tube connected with the neck of the jar, from the cistern B, a hole in the cover of which allows air to enter it as the gas flows out; the flame of each taper will gradually expire as the surface of the gas rises in the jar.

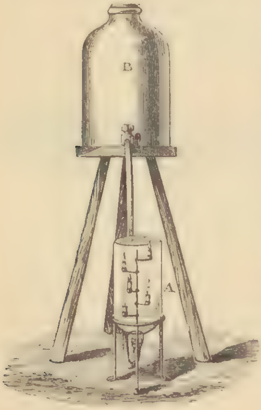

Fig. 70.

A jar of oxygen may be placed over a jar of carbonic acid gas, as shown in fig. 53, and a taper let down through the oxygen, in which it will burn brilliantly, into the carbonic acid gas, which extinguishes it, and if it be quickly raised again into the oxygen, it will rekindle with a slight detonation. This alternate extinction and rekindling may be repeated several times.

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* All gases which take no part in combustion may extinguish flame, even in the presence of air, by absorbing heat and reducing the temperature below the burning point.

On account of this extinguishing power of carbonic acid gas, a taper cannot continue to burn in a confined portion of air until it has exhausted the oxygen, but only until its combustion has produced a sufficient quantity of carbon dioxide to extinguish the flame.*

To demonstrate this, advantage may be taken of the circumstance that phosphorus will continue to burn in spite of the presence of carbonic acid gas. Upon the stand A (fig. 71) a small piece of phosphorus is placed, and a taper is attached to the stand by a wire. The cork B fits air-tight into the jar, and carries a piece of copper wire bent so that it may be heated by the flame of the taper. A little water is poured into the plate to prevent the entrance of any fresh air. If the taper be kindled, and the jar placed over it, the flame will soon die out; and on moving the jar so that the hot wire may touch the phosphorus, its combustion will show that a considerable amount of oxygen still remains.

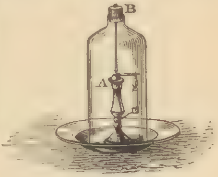

Fig. 71.

In the same manner, an animal can breathe a confined portion of air only until he has charged it with so much carbonic acid gas that the hurtful effect of this gas begins to be felt, a considerable quantity of oxygen still remaining.

If the air contained in the jar A (fig. 72), standing over water, be breathed two or three times through the tube B, a painful sense of oppression will soon be felt in consequence of the accumulation of carbonic acid gas. The air may thus be charged with 10 volumes of carbonic acid gas in 100 volumes, the oxygen becoming reduced to about one-half its original quantity. By immersing a deflagrating spoon C, containing a piece of burning phosphorus, and having a lighted taper attached, it may be shown that, although there is enough carbonic acid gas to extinguish the taper, the oxygen is not exhausted, for the phosphorus continues to burn rapidly.

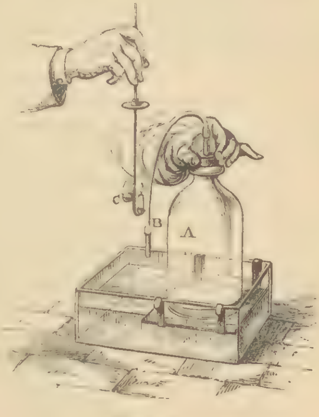

Fig. 72.

Carbonic acid gas is not poisonous when taken into the stomach, but acts most injuriously when breathed, by offering an obstacle to that escape of carbonic acid gas, by diffusion, from the blood of the venous circulation in the lungs, and its consequent replacement by the oxygen necessary to arterial blood. Any hindrance to this interchange must impede respiration, and such hindrance would, of course, be afforded by carbonic acid gas present in the air inhaled, in proportion to its quantity. The difference in constitution and temperament in individuals makes it impossible that any exact general rule should be laid down as to the precise quantity of carbonic acid gas which may be present in air without injury to respiration, but it may be safely asserted that it is not advisable to breathe for any length of time in air containing more than $\frac{1}{1000}$th (0.1 per cent.) of its volume of carbonic acid gas. The air of a room contains too much carbonic acid gas if half a measured ounce of lime-water becomes turbid when shaken in a half-pint bottle of the air.

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* When the taper is extinguished, the air contains in 100 volumes $18\frac{3}{4}$ volumes of oxygen and $2\frac{1}{4}$ volumes of carbonic acid gas.

There appears to be no *immediate* danger, however, until the carbonic acid gas amounts to $\frac{1}{200}$th (0.5 per cent.), when most persons are attacked by the languor and headache attending the action of this gas. A larger proportion of carbonic acid gas produces insensibility, and air containing $\frac{1}{12}$th of its volume causes suffocation. The danger in entering old wells, cellars, and other confined places, is due to the accumulation of this gas, either exhaled from the earth or produced by decay of organic matter. The ordinary test applied to such confined air by introducing a candle is only to be depended upon if the candle burns as brightly in the confined space as in the external air; should the flame become at all dim, it would be unsafe to enter, for experience has shown that combustion may continue for some time in an atmosphere dangerously charged with carbonic acid gas.

The accidents from *choke damp* and *after damp* in coal mines, and from the accumulation, in brewers' and distillers' vats, of the carbonic acid gas resulting from fermentation, are also examples of its fatal effect.

The air issuing from the lungs of a man at each expiration contains from 3.5 to 4 volumes of carbonic acid gas in 100 volumes of air, and could not, therefore, be breathed again without danger. The total amount of carbonic acid gas evolved by the lungs and skin amounts to about 0.7 cubic foot per hour. Adding this to the carbonic acid gas already present in the air, the total should be distributed through at least 3500 cubic feet, in order that it may be breathed again with perfect safety, that is, that the CO_2 should not exceed 0.06 per cent. by volume. Hence the necessity for a constant supply of fresh air by ventilation, to dilute the carbonic acid gas to such an extent that it may cease to impede respiration. This becomes the more necessary where an additional quantity of carbonic acid gas is supplied by candles or gas-lights. An ordinary gas burner consumes at least 3 cubic feet of gas per hour, and produces about 1.7 cubic foot of carbonic acid gas. Fortunately, a natural provision for ventilation exists in the circumstance that the processes of respiration and combustion, which contaminate the air, also raise its temperature, thus diminishing its specific gravity by expansion, and causing it to ascend and give place to fresh air. Hence the vitiated air always accumulates near the ceiling of an apartment, and it becomes necessary to afford it an outlet by opening the upper sash of the window, since the chimney ventilates immediately only the lower part of the room.

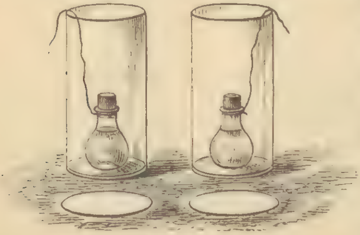

Fig. 73.

These principles may be illustrated by some very simple experiments.

Two quart jars (fig. 73) are filled with carbonic acid gas, and after being tested with a taper, a 4 oz. flask is lowered into each, one flask containing cold and the other hot water. After a few minutes the jar with the cold flask will still contain enough carbonic acid gas to extinguish the taper, whilst the air in the other jar will support combustion brilliantly.

A tall stoppered glass jar (fig. 74) is placed over a stand, upon which three lighted tapers are fixed at different heights. The vitiated air, rising to the top of the jar, will extinguish the uppermost taper first, and the others in succession. By quickly removing the stopper and raising the jar a little before the lowest taper has expired, the jar will be ventilated and the taper revived.

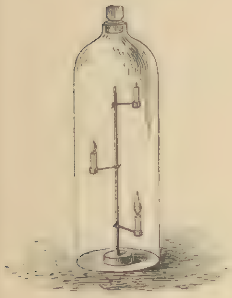

Fig. 74.

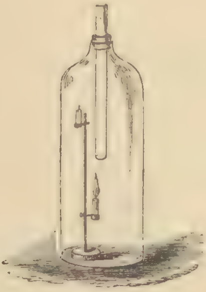

Fig. 75.

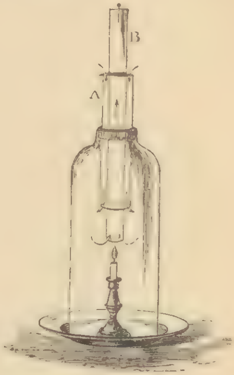

Fig. 76.

A similar jar (fig. 75), with a glass chimney fixed into the neck through a cork or piece of vulcanised tubing, is placed over a stand with two tapers, one of which is near the top of the jar, and the other beneath the aperture of the chimney; if a crevice for the entrance of air be left between the jar and the table, the lower taper will continue to burn indefinitely, whilst the upper one will soon be extinguished by the carbonic acid gas accumulating around it.

In ordinary apartments, the incidental crevices of the doors and windows are depended upon for the entrance of fresh air, whilst the contaminated air passes out by the chimney; but in large buildings special provision must be made for the two air currents. In mines this becomes the more necessary, since the air receives much additional contamination by the gases (marsh-gas and carbon dioxide) evolved from the workings, and by the smoke occasioned in blasting with gunpowder. Mines are generally provided with two shafts for ventilation, under one of which (the *upcast* shaft) a fire is maintained to produce the upward current, which carries off the foul air, whilst the fresh air descends by the other (*downcast* shaft). The current of fresh air is forced by wooden partitions to divide itself, and to pass through every portion of the workings.

The operation of such provisions for ventilation is easily exhibited.

A tall jar (fig. 76) is fitted with a ring of cork, carrying a wide glass chimney (A). If this be placed over a taper standing in a plate of water, the accumulation of vitiated air will soon extinguish the taper; but if a second chimney (B), supported in a wire ring, be placed within the wide chimney, fresh air will enter through the interval between the two, and the smoke from a piece of brown paper will demonstrate the existence of the two currents, as shown by the arrows.

A small box (fig. 77) is provided with a glass chimney at each end. In one of these (B), representing the upcast shaft, a lighted taper is suspended. A piece of smoking brown paper may be held in each chimney to show the direction of the current. On closing A with a glass plate, the taper in B will be extinguished, the entrance of fresh air being prevented. By breathing gently into A the taper will also be extinguished. The experiment may be varied by pouring carbon dioxide and oxygen alternately into A, when the taper will be extinguished and rekindled by turns.

A pint bell-jar (fig. 78) is placed over a taper standing in a tray of water. If a chimney (a common lamp-glass) be placed on the top of the jar, the flame of the taper will gradually die out, because no provision exists for the establishment of the two currents, but on dropping a piece of tinplate or cardboard into the chimney so as to divide it, the taper will be revived, and the smoke from the brown paper will distinguish the upcast from the downcast shaft.

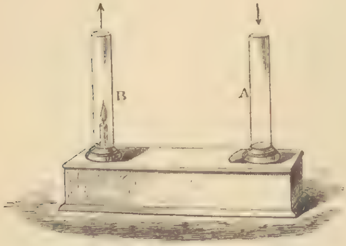

Fig. 77.

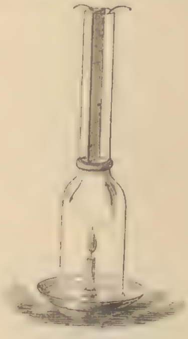

Fig. 78.

If a little water be poured into a wide-mouthed bottle of carbonic acid gas, and the bottle be then firmly closed by the palm of the hand, it will be found, on shaking the bottle violently, that the gas is absorbed, and the palm of the hand is sucked into the bottle. The presence of carbonic acid in the solution may be proved by pouring it into lime-water, in which it will produce a precipitate of calcium carbonate, redissolved by a further addition of the solution of carbonic acid.

One pint of water shaken in a vessel containing carbonic acid gas, at the ordinary pressure of the atmosphere, will dissolve about one pint of the gas, equal in weight to nearly 16 grains. If the gas be confined in the vessel under a pressure equal to twice or thrice that of the atmosphere —that is, if twice or thrice the quantity of gas be compressed into the same space—the water will still dissolve one pint of the gas, but the weight of this pint will now be twice or thrice that of the pint of uncompressed gas, so that the water will have dissolved 32 or 48 grains of the gas, accordingly as the pressure had been doubled or trebled. As soon, however, as the pressure is removed, the compressed carbonic acid gas will resume its former state, with the exception of that portion which the water is capable of retaining in solution under the ordinary pressure of the atmosphere. Thus if the water had been charged with carbonic acid gas under a pressure equal to thrice that of the atmosphere, and had therefore absorbed 48 grains of the gas, it would only retain 16 grains when the pressure was taken off, allowing 32 grains to escape in minute bubbles, producing the appearance known as *effervescence*. This affords an explanation of the properties of soda-water, which is prepared by charging water with carbonic acid gas under considerable pressure, and rapidly confining it in strong bottles. As soon as the resistance offered by the cork to the expansion of the gas is removed, the excess above that which the water can hold in solution at the ordinary pressure of the air, escapes with effervescence. In a similar manner the waters of certain springs become charged with carbonic acid gas, under high pressure, beneath the surface of the earth, and when, upon their rising to the surface, this pressure is removed, the excess escapes with effervescence, giving rise to the sparkling appearance and sharp flavour which render spring water so agreeable. On the other hand, the waters of lakes and rivers are usually flat and insipid, because they hold in solution so small a quantity of carbonic acid gas.

The solution of carbon dioxide in water is believed by many chemists to contain the true *carbonic acid* or *hydric carbonate*, H_2CO_3, for $CO_2 + H_2O = H_2CO_3$, but there is no direct evidence in support of this view.

The sparkling character of champagne, bottled beer, &c., is due to the presence in these liquids of a quantity of carbonic acid gas which has been generated by fermentation, subsequent to bottling, and has therefore been retained in the liquid under pressure. In the case of Seidlitz powders and soda-water powders, the effervescence caused by dissolving them in water is due to the disengagement of carbonic acid gas, by the action of the tartaric acid, which composes one of the powders, upon the bicarbonate of soda, producing tartrate of soda and carbonic acid gas. In the dry state these powders may be mixed without any chemical change, but the addition of water immediately causes the effervescence. *Baking powders* are mixtures of this kind, being used for imparting lightness and porosity to bread and cakes, by distending the dough with bubbles of carbonic acid gas.

The solubility of carbonic acid in water is of great importance in the chemistry of nature; for this acid, brought down from the atmosphere dissolved in rain, is able to act chemically upon rocks, such as granite, which contain alkalies—the carbonic acid attacking these, and thus slowly disintegrating or crumbling down the rock, an effect much assisted by the mechanical action of the expansion of freezing water in the insterstices of the rock. It appears that soils are thus formed by the slow degradation of rocks, and when these soils are capable of supporting plants, the solution of carbonic acid is again of service, not only as a direct food, by providing the plant with carbon through its roots, but as a solvent for certain portions of the mineral food of the plant (such as calcium phosphate), which pure water could not dissolve, and which the plant cannot take up except in the dissolved state.

59. *Liquefaction of carbonic acid gas.*—Although carbon dioxide retains the state of gas under all temperatures and pressures to which it is commonly exposed, it is capable of assuming the liquid and even the solid state.

At about the ordinary temperature (63° F.) carbonic acid gas is condensed, by a pressure of 54 atmospheres (800 lbs. per square inch), to a colourless liquid of sp. gr. 0.83 (water = 1), and at a temperature of $-70°$ F. (70° below the zero, or 102° below the freezing point F.) becomes a transparent mass of solid carbon dioxide resembling ice.

If the temperature of the gas be reduced to 32° F. a pressure of 35 atmospheres only will suffice to liquefy it.

The experiments of Andrews upon the liquefaction of carbon dioxide show that, in causing the liquefaction of gases, increase of pressure is not always equivalent to reduction of temperature, but that there exists a particular temperature for each gas above which no amount of pressure is able to liquefy it, and at this particular temperature, the *critical point*, the gas is wavering between the gaseous and the liquid state, so that "the gaseous and liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle, that the passage shall nowhere present any interruption or breach of continuity." It was found to be impossible to liquefy carbon dioxide above a temperature of 88° F. (31° C.) even by a pressure of 109 atmospheres; but, at this high pressure the gas ceased to obey the law that the volume of a gas is inversely as the pressure, for instead of occupying $\frac{1}{109}$ of its original volume, it had been reduced to $\frac{1}{430}$. On cooling the gas thus compressed, it liquefied suddenly, and not gradually as in the case of a vapour under ordinary pressure. The gas in this condition, when subjected to very small variations of temperature or pressure, exhibits curious flickering movements, resembling the effect produced by the ascent of columns of heated air through colder strata. Even at 55° F., a pressure of 48.89 atmospheres reduced the gas (not to $\frac{1}{49}$ but) to $\frac{1}{81}$ of its original volume without liquefying it, but at this point an additional pressure of only $\frac{1}{20}$ atmosphere suddenly liquefied one-half of the gas.*

A small specimen of liquid carbon dioxide is easily prepared. A strong tube of green glass (A, fig. 79) is selected, about 12 inches long, $\frac{5}{16}$ inch diameter in the bore, and $\frac{1}{10}$ inch thick in the walls. With the aid of the blowpipe flame this tube is softened and drawn off at about an inch from one end, as at B, which is thus closed (C). This operation should be performed slowly, in order that the closed end may not be much thinner than the walls of the tube. When the tube has cooled, between 30 and 40 grs. of powdered bicarbonate of ammonia (ordinary sesquicarbonate which has crumbled down) are tightly rammed into it with a glass rod. This part of the tube is then surrounded with a few folds of wet blotting-paper to keep it cool, and the tube is bent, just beyond the carbonate of ammonia, to a somewhat obtuse angle (D). The tube is then softened at about an inch from the open end, and drawn out to a narrow neck (E), through which a measured drachm of oil of vitriol is poured down a funnel-tube, so as not to soil the neck, which is then carefully drawn out and sealed by the blowpipe flame, as at F. The empty space in the tube should not exceed $\frac{1}{6}$ cubic inch.

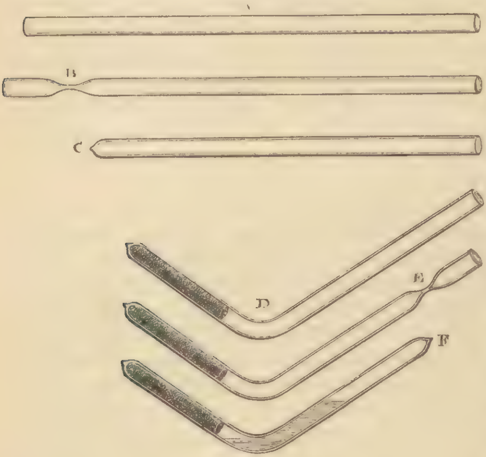

Fig. 79.

When the tube is thoroughly cold, it is suspended by strings in such a position that the operator, having retired behind a screen at some distance, may reverse the tube, allowing the acid to flow into the limb containing the carbonate of ammonia; or the tube may be fixed in a box which is shut up, and reversed so as to bring the tube into the required position.

If the tube be strong enough to resist the pressure, it will be found, after a few hours, that a layer of liquid carbon dioxide has been formed upon the surface of the solution of ammonium sulphate. By cooling the empty limb in a mixture of pounded ice and salt, or of hydrochloric acid and sodium sulphate, the liquid can be made to distil itself over into this limb, leaving the ammonium sulphate in the other.

Fig. 80 represents Thilorier's apparatus for the preparation of several pints of liquid carbon dioxide: *g* is a strong *wrought-iron generator* of gas in which 2 lbs. of bicarbonate of soda are well stirred with 4 pints of water at 100° F. Half a pint of oil of vitriol is poured into a brass tube which is dropped upright into the generator, as shown by the dotted lines in the figure, which also indicate the level of the liquid in the generator. The head of the generator is then firmly screwed on, with the help of the spanners represented in the figure, and the stopcock* firmly closed by turning the wheel *w*. The generator is then turned over and over on its trunnions resting upon the stand *s*, for ten minutes, so that the whole of the sulphuric acid may be mixed with the solution of bicarbonate of soda. The generator is then connected, by the copper tube *t*, with the strong wrought-iron *receiver r*, the stopcock of which is attached to a tube passing down to the bottom of the vessel. The stopcock of the receiver is then opened, by turning the wheel *v*, and afterwards that of the generator.

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* The knowledge of the critical point of CO_2 enabled Hartley to establish the existence of liquid CO_2 in the minute cavities visible in microscopic sections of minerals.

The condensed gas then passes over into the receiver. After two or three minutes the stopcocks are again closed, the generator detached, the waste gas blown out through the stopcock, the head unscrewed, and the generator emptied and recharged. After the operation has been repeated three times, the pressure in the receiver will be found to have liquefied some of the carbon dioxide, and after seven charges, the receiver is nearly filled with the liquid acid. The tube *t* is then unscrewed from the receiver, and replaced by the nozzle *n*. If the stopcock be then slightly opened, a stream of the liquid will be forced up the tube, and, issuing into the air, will congeal by its own evaporation into an opaque white spray of solid carbon dioxide.

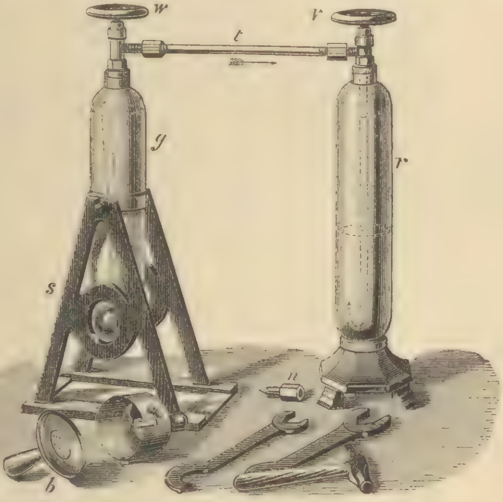

Fig. 80.—Liquefaction of carbonic acid gas.

In order to collect the solid, the box shown at *b* is employed. This is made of brass, and furnished with strong flanges by which the cover is secured to it. The handles of the box are made of wood or gutta-percha, and are hollow, with brass tubes passing through them to allow of the escape of gas, the ends of the tubes within the box being covered by perforated plates which prevent the escape of the solid. The box and its cover having been fitted together, the nozzle of the receiver *r* is inserted into a short tube projecting from the side of the box, and whilst one operator holds the box firmly by the handles, another gradually opens the stopcock by turning the wheel *v*. A stream of the liquid is at once forced into the box, where it strikes against a curved brass plate arranged so as to force it to pass all around the inside of the box; about seven-eighths of it evaporate as gas, which rushes out through the tubular handles, and the rest is found in the box in a solid state resembling snow. It should be quickly shaken on to a sheet of paper, and emptied into a beaker placed within a larger beaker, the interval being filled up by flannel. By covering the beaker with a dial glass, the solid may be kept for some time. The box becomes intensely cold, and condenses the moisture of the air to a thick layer of hoar-frost, and if it be dipped into water it becomes coated with ice.

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* These stopcocks are steel screws with conical points fitting into gun-metal sockets. Leaden washers are employed to secure the tightness of the joints between the iron vessels and their heads, which are made of gun-metal.

The solid carbon dioxide evaporates without melting, for its melting point is – 85° F., and its own evaporation keeps it at – 125° F. It produces a sharp sensation of cold when placed upon the hand, and if pressed into actual contact with the skin causes a painful frost-bite. Its rapid evaporation may be shown by placing a few fragments on the surface of water in the globe (fig. 81), which has a tube passing down to the bottom, through which the pressure of the carbonic acid gas forces the water to a considerable height.

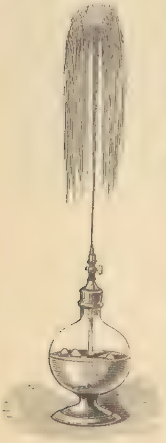

Fig. 81.

The solid carbon dioxide is soluble in ether, and it evaporates from this solution far more rapidly, because the liquid is a better conductor of heat than the highly porous solid, and abstracts heat more rapidly from surrounding objects.

If a layer of ether be poured upon water, and some solid carbon dioxide be thrown into it, the water is covered with a layer of ice.

On immersing the bulb of a thermometer into the solution of solid carbon dioxide in ether, the mercury becomes solid, and the bulb may be hammered out into a disk.

By placing a piece of filter-paper in an evaporating dish, pouring a pound or so of mercury into it, immersing a wire turned into a flat spiral at the end, covering the mercury with ether, and throwing in some solid carbon dioxide, the mercury may soon be frozen into a cake. If this be suspended by the wire in a vessel of water, the mercury melts, descending in silvery streams to the bottom of the vessel, leaving a cake of ice on the wire, with icicles formed during the descent of the mercury. This experiment is rendered more effective by using an inverted gas-jar, to the neck of which is attached by a perforated cork, a test-tube to catch the mercury. The round lid of a cardboard box gives a nice disk of frozen mercury.

Even in a red-hot vessel, with prompt manipulation, the mercury may be solidified by the solution of solid carbon dioxide in ether. For this purpose a platinum dish is heated to redness over a large Bunsen burner, a few lumps of carbon dioxide are thrown into it, upon these is held a copper or platinum dish containing the mercury, in which is also held a wire to serve as a handle for withdrawing the mercury. Some more carbon dioxide is thrown upon the mercury, and ether is spirted on to it from a small washing-bottle. One or two additions of the carbon dioxide and ether alternately will freeze the mercury, which may be withdrawn from the flames by the wire handle.

The temperature produced by the evaporation of the solid carbon dioxide dissolved in ether is estimated at – 150° F., or nearly – 100° C.

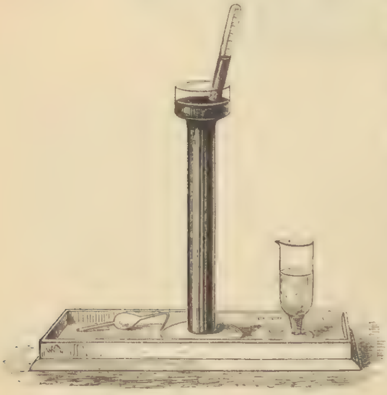

Fig. 82.

60. Carbonic acid gas may be separated from most other gases by the action of potash, which absorbs it, forming potassium carbonate. The proportion of carbonic acid gas is inferred, either from the diminution in volume suffered by the gas when treated with potash, or from the increase of weight of the latter.

In the former case the gas is carefully measured over mercury (fig. 82), with due attention to temperature and barometric pressure, and a little concentrated solution of potash is thrown up through a curved *pipette* or syringe, introduced into the orifice of the tube beneath the surface of the mercury. The tube is gently shaken for a few seconds to promote the absorption of the gas, and, after a few minutes' rest, the diminution of volume is read off. Instead of solution of potash, damp potassium hydrate in the solid state is sometimes introduced, in the form of small sticks or balls attached to a wire. To determine the weight of carbonic acid gas in a gaseous mixture, the latter is passed through a bulb-apparatus (H, fig. 55), containing a strong solution of potash, and weighed before and after the passage of the gas. When the proportion of carbonic acid in the gas is small, it is usual to attach to the bulb-apparatus a little tube, containing solid potash, or calcium chloride, or pumice-stone moistened with sulphuric acid, for the purpose of retaining any vapour of water which the large volume of unabsorbed gas might carry away in passing through the solution of potash.

61. *Salts formed by carbonic acid.*—Although so ready to combine with the alkalies and alkaline earths (as shown in its absorption by solution of potash and by lime-water), carbonic acid must be classed among the weaker acids. It does not neutralise the alkalies completely, and it may be displaced from its salts by most other acids. Its action upon the colouring matter of litmus is feeble and transient. If a solution of carbonic acid be added to blue infusion of litmus, a wine-red liquid is produced, which becomes blue again when boiled, losing its carbonic acid; whilst litmus reddened by sulphuric, hydrochloric, or nitric acid, acquires a brighter red colour, which is permanent on boiling.

With each of the alkalies carbonic acid forms two well-defined salts, the *carbonate* and *bicarbonate*. Thus, the carbonates of potassium and sodium are represented by the formulæ, K_2CO_3 and Na_2CO_3, whilst the bicarbonates are $KHCO_3$ and $NaHCO_3$. The existence of the latter salts would favour the belief in the existence of the compound H_2CO_3, although no such combination has yet been obtained in the separate state. Perfectly dry carbonic acid gas is not absorbed by pure quicklime (CaO), until it is heated to a certain point.

Two hard glass tubes closed at one end, and bent as in fig. 83, are perfectly dried, and filled, over mercury, with well-dried carbonic acid gas. Fragments of lime are taken, whilst red hot, out of a crucible, cooled under the mercury, inserted into the tubes, and transferred to the upper end. No absorption of the gas takes place, though the tubes be left for some days; but if one of them be heated by a Bunsen burner, the absorption of carbonic acid gas takes place rapidly, and the mercury is forced up into the tube.

The formula H_2CO_3 represents carbonic acid as a *dibasic* acid, that is, an acid containing two atoms of hydrogen which may be replaced by metals.

Carbonates may be *normal*, *acid*, or *basic*. A normal carbonate is one in which all the hydrogen in H_2CO_3 is replaced by a metal or metals, as in sodium carbonate, Na_2CO_3, and calcium carbonate, $CaCO_3$.

An acid carbonate is one in which only half of the hydrogen is replaced by a metal, as in hydrosodium carbonate, $NaHCO_3$. A basic carbonate is a normal carbonate in combination with a hydrate of the metal, as in *white lead*, basic lead carbonate, $2PbCO_3.Pb(HO)_2$.

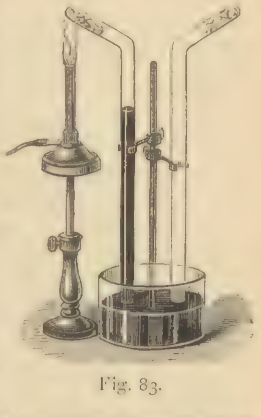
Fig. 83.

62. To demonstrate the presence of carbon in carbonic acid gas, a pellet of potassium is introduced into a bulb tube, through which a current of carbonic acid gas (dried by passing through oil of vitriol, or over chloride of calcium) is flowing, and the heat of a spirit-lamp is applied to the bulb. The metal will soon burn in the gas, which it robs of its oxygen, leaving the carbon as a black mass in the bulb (fig. 84). The potassium remains in the form of potassium carbonate, $3CO_2 + K_4 = 2K_2CO_3 + C$. If slices of sodium be

arranged in a test-tube in alternate layers with dried chalk (calcium carbonate), and strongly heated with a spirit-lamp, vivid combustion will ensue, and much carbon will be separated ($CaCO_3 + Na_4 = CaO + 2Na_2O + C$).

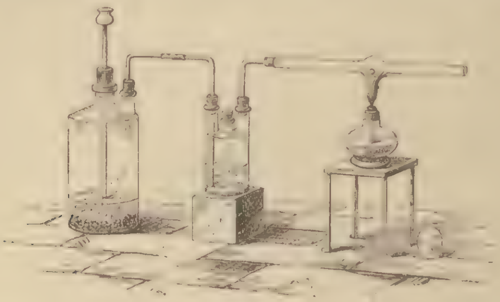

Fig. 84.

63. Carbonic Oxide ($CO = 28$ parts by weight = 2 volumes).—Other metals, which are not endowed with so powerful an attraction for oxygen, do not carry the decomposition of carbon dioxide to its final limit; thus, iron and zinc* at a high temperature will only deprive the gas of one half of its oxygen, a result which may also be brought about at a red heat by carbon itself. If an iron tube filled with fragments of charcoal be heated to redness in a furnace (fig. 9), and carbonic acid gas be transmitted through it, it will be found, on collecting the gas which issues from the other extremity of the tube, that on the approach of a taper, it takes fire, and burns with a beautiful blue lambent flame, similar to that which is often observed to play over the surface of a clear fire. Both flames, in fact, are due to the same gas, and in both cases this gas results from the same chemical change, for, in the tube, the carbonic acid gas yields half of its oxygen to the charcoal, both becoming converted into carbonic oxide; $CO_2 + C = 2CO$. In the fire, the carbonic acid gas is formed by the combustion of the carbon of the fuel in the oxygen of the air entering at the bottom of the grate; and this carbonic acid gas, in passing over the layer of heated carbon in the upper part of the fire, is partly converted into carbonic oxide, which inflames when it meets with the oxygen in the air above the surface of the fuel, and burns with its characteristic blue flame, reproducing carbon dioxide. The carbonic oxide occupies twice the volume of the carbon dioxide from which it was produced.

This conversion of carbon dioxide into carbonic oxide is of great importance on account of its extensive application in metallurgic operations. It is often desirable, for instance, that a flame should be made to play over the surface of an ore placed on the bed or hearth of a reverberatory furnace (fig. 85). This object is easily attained when the coal affords a large quantity of inflammable gas; but with anthracite coal, which burns with very little flame, and is frequently employed in such furnaces, it is necessary to pile a high column of coal upon the grate, so that the carbon dioxide formed beneath may be converted into carbonic oxide in passing over the heated coal above, and when this gas reaches the hearth of the furnace, into which air is admitted, it burns with a flame which spreads over the surface of the ore. The temperature of the flame of carbonic oxide burning in air is estimated at about 2000° C.

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* Magnesium also reduces carbon dioxide to carbonic oxide.

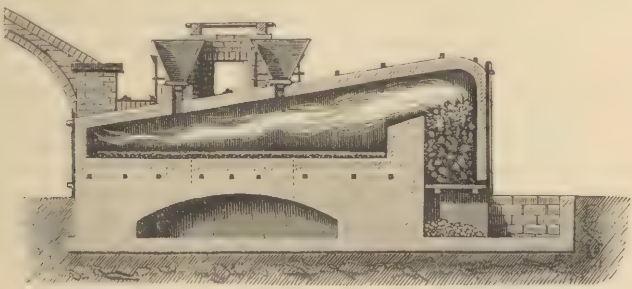

Fig. 85.—Reverberatory furnace for copper smelting.

The attraction of carbonic oxide for oxygen is turned to account in removing that element from combination with iron in its ores, as will be seen hereafter.

Since the heat produced in combustion is proportional to the oxygen consumed (p. 26), the conversion of C into CO_2 should produce twice as much heat as its conversion into CO. When C, in the form of charcoal, burns to form CO_2, each gramme of C produces 8080 gramme units of heat; or C, 12 grms., + O_2, 32 grms., = CO_2 + 96960 units of heat. Now carbon cannot be burned directly to form CO, but when CO burns to form CO_2, 1 grm. of CO produces 2403 units of heat; or CO, 28 grms., + O, 16 grms., = CO_2 + 67284 units of heat. In the first equation, 16 grms. of O produce 48480 units, and in the second 67284 units of heat. But in the first case, solid carbon is converted into gas, a change of state which must absorb much of the heat produced. If the C were in the state of gas to begin with, in both cases, we should have O, 16 grms., + C, 12 grms., = CO + 67284 units of heat, and O_2, 32 grms., + C, 12 grms., = CO_2 + 134568 units of heat, so that 1 grm. of C would give 11214 units of heat when burned to CO_2. But when 1 grm. of solid C burns to CO_2 it gives only 8080 units of heat; hence 11214 − 8080, or 3134 units, represent the heat required to convert 1 grm. of solid carbon into gas.

64. Carbonic oxide is very poisonous; and it appears that the accidents which too frequently occur from burning charcoal or coke in braziers and chafing-dishes in close rooms, result from the poisonous effects of the small quantity of carbonic oxide which is produced and escapes combustion, since the amount of carbonic acid gas thus diffused through the air is not sufficient, in most cases, to account for the fatal result. The carbonic oxide formed in cast-iron stoves diffuses through the hot metal into the air of a room.

65. The knowledge of the poisonous character of carbonic oxide gave rise a few years since to considerable apprehension, when it was proposed to employ this gas in Paris for purposes of illumination. The character of the flame of carbonic oxide would appear to afford little promise of its utility as an illuminating agent; but that it is possible so to employ it is easily demonstrated by kindling a jet of the gas which has been passed through a wide tube containing a little cotton moistened with rectified coal naphtha (benzene), when it will be found to burn with a very luminous flame. The carbonic oxide destined to be employed for illuminating purposes was prepared by passing steam over red-hot coke or charcoal, when a highly inflammable gas was obtained, containing carbon dioxide, carbonic oxide and hydrogen; $4H_2O + C_3 = CO_2 + 2CO + H_8$.

Since neither hydrogen nor carbonic oxide burns with a luminous flame, this gas was next passed into a vessel containing red-hot coke, over which melted resin was allowed to trickle. The action of heat upon the resin gave rise to the production of vapours similar to that of the benzene employed in the above experiment, and which, in like manner, conferred considerable illuminating power upon the gas.

The decomposition of steam by red-hot carbon is also taken advantage of in order to procure a flame from anthracite coal when employed for heating boilers. The coal being burnt on *fish-bellied* bars, beneath which a quantity of water is placed, the radiated heat converts the water into steam, which is carried by the draught into the fire, where it furnishes carbonic oxide and hydrogen, both capable of burning with flame under the bottom of the boiler. The temperature of the bars is also thus reduced, so that they are not so much injured by the intense heat of the glowing fuel.

66. Carbonic oxide, unlike carbon dioxide, is nearly insoluble in water. It is even lighter than air, its specific gravity being 0.967. In its chemical relations it is an indifferent oxide, that is, it has neither acid nor basic properties. It has been liquefied by the cold produced by its own expansion under a compression of 300 atmospheres at $-29°$ C.; the liquid boils, under atmospheric pressure, at $-193°$ C., which is also the boiling point of nitrogen.

67. A very instructive process for obtaining carbonic oxide, consists in heating crystallised oxalic acid with three times its weight of oil of vitriol. If the gas be collected over water (fig. 86), and one of the jars be shaken with a little lime-water, the milkiness imparted to the latter will indicate abundance of carbon dioxide; whilst, on removing the glass plate, and applying a light, the carbonic oxide will burn with its characteristic blue flame. The gas thus obtained is a mixture of equal volumes of carbonic oxide and carbonic acid gases. Crystallised oxalic acid is represented by the formula $C_2H_2O_4.2Aq.$, and if the water of crystallisation be left out of consideration, its decomposition may be represented by the equation $C_2H_2O_4 = H_2O + CO + CO_2$, the change being determined by the attraction of the oil of vitriol for water. To obtain pure carbonic oxide, the mixture of gases must be passed through a bottle containing solution of potash, to absorb the carbonic acid gas (fig. 87).

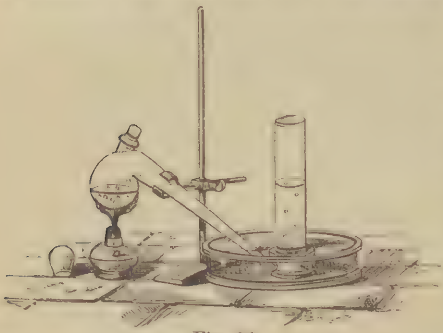

Fig. 86.

But pure carbonic oxide is much more easily obtained by the action of sulphuric acid upon crystallised potassium ferrocyanide (yellow prussiate of potash) at a moderate heat. Since the gas contains small quantities of sulphurous and carbonic acid gases, it must be passed through solution of potash if it be required perfectly pure. The chemical change which occurs in this process is expressed thus:—

$$\underset{\text{Potassium ferrocyanide.}}{K_4C_6N_6Fe} + 6H_2O + 6H_2SO_4 = 6CO + \underset{\text{Potassium sulphate.}}{2K_2SO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4}.$$

Ten grammes of crystallised ferrocyanide, with 135 grammes of sulphuric acid (sp. gr. 1.84) and 13 grammes of water, will give about $3\frac{1}{2}$ litres of carbonic oxide.

If the boiling is continued after the evolution of CO has ceased, much sulphurous acid gas is disengaged ($2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + SO_2$).

68. To demonstrate the production of carbonic acid gas during the combustion of carbonic oxide, a jar of the gas is closed with a glass plate, and after placing it upon the table, the plate is slipped aside and a little lime-water quickly poured into the jar. On shaking, no milkiness indicative of carbonic acid gas should be perceived. The plate is then removed and the gas kindled. On replacing the plate and shaking the jar, an abundant precipitation of calcium carbonate will take place.

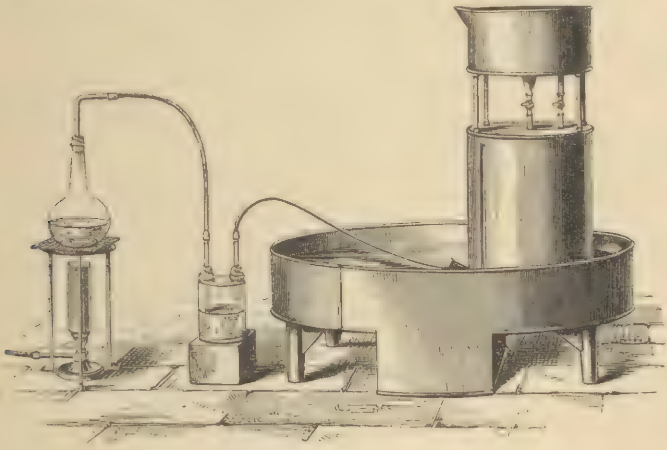

Fig. 87.—Preparation of carbonic oxide.

Carbonic oxide forms an explosive mixture with half its volume of oxygen; the remarkable observation has been made that if the mixture be absolutely free from vapour of water it does not explode on passing an electric spark through it.

When carbonic oxide is passed through a red-hot porcelain tube, a portion of it is decomposed into carbonic acid gas and carbon; and when the experiment is conducted without special arrangements, the carbonic oxide is reproduced as the temperature of the gas falls. But by passing through the centre of the porcelain tube a brass tube, through which cold water is kept running, the decomposition has been demonstrated by the deposition of carbon upon the cooled tube, and by collecting the carbonic acid gas formed. Carbonic acid gas is also decomposed by intense heat into carbonic oxide and oxygen; but if these gases be allowed to cool down slowly in contact, they recombine. The gas drawn from the hottest region of a blast-furnace (see *Iron*), and rapidly cooled, so as to prevent recombination, was found to contain both carbonic oxide and oxygen. According to Brodie, carbonic acid gas is partially decomposed into carbonic oxide and oxygen by electric inductive discharge (p. 57), and $\frac{3}{4}$ of the oxygen assumes the form of ozone.

By passing a pellet of phosphorus up into carbonic acid gas, over mercury, in a eudiometer, and passing electric sparks for some days, the gas has been entirely decomposed, an equal volume of carbonic oxide being left.

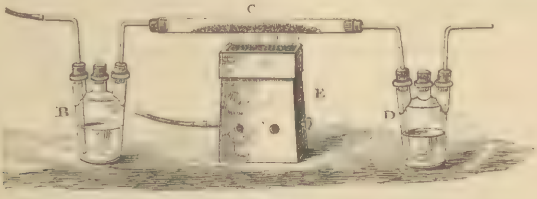

Fig. 88.—Reduction of oxide of copper by carbonic oxide.

The reducing action of carbonic oxide upon metallic oxides, at high temperatures, may be illustrated by passing the pure gas from a bag or gas-holder, first through a bottle of lime-water (B, fig. 88), to prove the absence of carbonic acid gas, then over oxide of copper, contained in the tube C, and afterwards again through lime-water in D. When enough gas has been passed to expel the air, heat may be applied to the tube by the gauze-burner E, when the formation of carbonic acid gas will be immediately shown by the second portion of lime-water, and the black oxide of copper will be reduced to red metallic copper.

If precipitated peroxide of iron be substituted for oxide of copper, iron in the state of black powder will be left, and if allowed to cool in the stream of gas, will take fire when it is shaken out into the air, becoming reconverted into the peroxide (*iron pyrophorus*).

Carbonic oxide is absorbed by potassium hydrate at 100° C., potassium *formate* being produced; $CO + KHO = KCHO_2$. If carbonic oxide be passed over soda-lime in a glass tube heated by a gas-furnace, sodium carbonate is formed, and hydrogen liberated; $CO + 2NaHO = Na_2CO_3 + H_2$.

69. *Composition by volume of carbonic oxide and carbon dioxide.*—When carbon burns in oxygen, the volume of the carbon dioxide produced is exactly equal to that of the oxygen, so that one volume of oxygen furnishes one volume of carbonic acid gas, or a molecule (two volumes, see p. 2) of carbonic acid gas contains two volumes of oxygen.

When one volume of carbonic acid gas (containing one volume of oxygen) is passed over heated carbon, it yields two volumes of carbonic oxide; hence two volumes, or one molecule, of this gas contain one volume of oxygen.

Specific gravity (to H) of CO_2, *i.e.*, weight of one volume . .	22
Specific gravity (to H), or weight of one volume, of O . . .	16
Weight of carbon in one volume of CO_2	6

Hence, a molecule, two volumes or 44 parts by weight, of CO_2, contains 12 parts by weight of carbon.

Specific gravity (to H), or weight of one volume, of CO = 14

Weight of two volumes of CO	28
,, one volume of O	16
Weight of carbon in two volumes (or one molecule) of CO . .	12

70. The *atomic weight* of carbon is taken as 12, since this is the smallest weight of carbon which can be found in two volumes of any of its gaseous compounds.

COMPOUNDS OF CARBON AND HYDROGEN.

71. No two other elements are capable of occurring in so many different forms of combination as carbon and hydrogen. The *hydrocarbons*, as their compounds are generally designated, include most of the inflammable gases which are commonly met with, and a great number of the essential oils, naphthas, and other useful substances. There is reason to believe that all these bodies, even such as are found in the mineral kingdom, have been originally derived from vegetable sources, and their history belongs, therefore, to the department of organic chemistry. The three simplest examples of such compounds will, however, be brought forward in this place to afford a general insight into the mutual relations of these two important elements.

72. *Acetylene** (C_2H_2 = 26 parts by weight = 2 vols.).—When very

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* Long known as *klumene*, having been obtained in 1836 by the action of water upon a compound containing carbon and potassium, produced during the preparation of that metal. The name acetylene is derived from the hypothetical radical acetyle (C_2H_3), to which acetylene bears the same relation as ethylene (C_2H_4) does to ethyle (C_2H_5).

intensely heated, carbon is capable of combining with hydrogen to form acetylene. The required temperature is procured by means of a powerful galvanic battery, to the terminal wires of which two pieces of dense carbon are attached, and the voltaic discharge is allowed to take place between them in an atmosphere of hydrogen. The experiment possesses little practical importance, because but little acetylene is formed in proportion to the force employed, but its theoretical interest is very great, since it is the first step in the production of organic substances by the direct synthesis of mineral elements; acetylene (C_2H_2) being convertible into olefiant gas (C_2H_4), this last into alcohol (C_2H_6O), and alcohol into a very large number of organic products.

Acetylene is constantly found among the products of the incomplete combustion and destructive distillation of substances rich in carbon; hence it is always present in small quantity in coal gas, and may be produced in abundance by passing the vapour of ether through a red-hot tube. The character by which acetylene is most easily recognised is that of producing a fine red precipitate in an ammoniacal solution of cuprous chloride (subchloride of copper).

The most convenient process for preparing a quantity of this precipitate, is that in which the acetylene is produced by the imperfect combustion taking place when a jet of atmospheric air is allowed to burn in coal gas.

An *adapter* (A, fig. 89), is connected at its narrow end with the pipe supplying coal gas. The wider opening is closed by a bung with two holes, one of which receives a piece of brass tube (B) about three-quarters of an inch wide and 7 inches long, and in the other is inserted a glass tube (C) which conducts the gas to the bottom of a *separating funnel* (D). The lower opening of the brass tube B is closed with a cork, through which passes the glass tube E connected with a gas-holder or bag containing atmospheric air. To commence the operation, the gas is turned on through the tube F, and when all air is supposed to be expelled, the tube E is withdrawn, together with its cork, and a light is applied to the lower opening of the brass tube, the supply of coal gas being so regulated that it shall burn with a small flame at the end of the tube. A feeble current of air is then allowed to issue from the tube E, which is passed up through the flame into the adapter, where the jet of air continues to burn in the coal gas,* and may be kept burning for hours with a little attention to the proportions in which the gas and air are supplied. A solution of cuprous chloride in ammonia is poured into the separating funnel through the lateral opening G, so that the imperfectly burnt gas may pass through it, when the cuprous acetylide is precipitated in abundance. When a sufficient quantity has been formed, or the copper solution is exhausted, the liquid is run out through the stopcock (H) on to a filter, and replaced by a fresh portion. The precipitate may be rinsed into a flask provided with a funnel tube and delivery tube, allowed to subside, the water decanted from it, and some strong hydro-

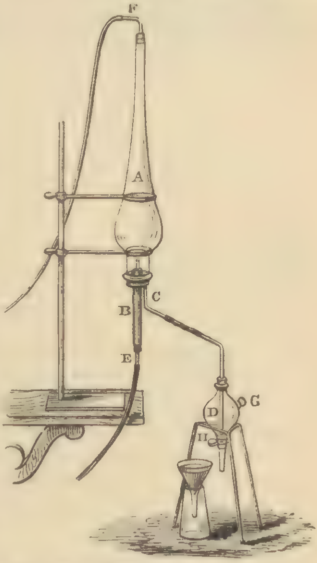

Fig. 89.—Preparation of cuprous acetylide.

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* It is advisable to attach a piece of thin platinum wire to the mouth of the glass tube to render the flame of the air more visible.

chloric acid poured in through the funnel. On heating, the acetylene is evolved, and may be collected, either over water, or more economically in a small gas-bag, or in a mercurial gas-holder. To obtain a pint of the gas, as much of the moist copper precipitate is required as will measure about 6 ounces after settling down. Such a quantity may be prepared in about six hours.

A solution of cuprous chloride suitable for this experiment is conveniently prepared in the following manner: —500 grains of black oxide of copper are dissolved in 7 measured ounces of common hydrochloric acid, in a flask, and boiled for about twenty minutes with 400 grains of copper in filings or fine turnings. The brown solution of cuprous chloride in hydrochloric acid, thus obtained, is poured into about 3 pints of water contained in a bottle; the white precipitate (cuprous chloride) is allowed to subside, the water drawn off with a siphon, and the precipitate rinsed into a 20-ounce bottle, which is then quite filled with water and closed with a stopper. When the precipitate has again subsided, the water is drawn off, and 4 ounces of powdered chloride of ammonium are introduced, the bottle being again filled up with water, closed and shaken. The cuprous chloride is entirely dissolved by the chloride of ammonium, but would be precipitated if more water were added. When required for the precipitation of acetylene, the solution may be mixed with about one-tenth of its bulk of strong ammonia (.880), which may be poured into the separating funnel (D) before the copper solution is introduced. Four measured ounces of the solution are sufficient for one charge, and yield, in three hours, about 3 measured ounces of the moist precipitate. The blue solution of ammoniacal cupric chloride, filtered from the red precipitate, may be rendered serviceable again by being shaken, in a stoppered bottle, with precipitated copper, prepared by reducing a solution of sulphate of copper, acidulated with hydrochloric acid, with a plate of zinc.

If the acetylene copper precipitate be collected on a filter, washed, and dried either by mere exposure to the air, or over oil of vitriol, it will be found to explode with some violence when gently heated, and it is said that the accidental formation of this compound in copper or brass pipes, through which coal gas passes, has occasionally given rise to explosions.

When acetylene is passed through solution of nitrate of silver, a white curdy precipitate is formed, resembling chloride of silver in appearance, but insoluble in ammonia (which turns it yellow) as well as in nitric acid. It may be obtained by allowing the imperfectly burnt gas from the apparatus in fig. 89 to pass through nitrate of silver.

It may be more easily prepared by suspending a funnel over a Bunsen burner which has caught fire inside the tube, and drawing the products of imperfect combustion, by means of an aspirator, through a solution of silver nitrate. This precipitate may also be used for the preparation of acetylene, by heating it with hydrochloric acid.

When this precipitate is washed and allowed to dry, it is violently explosive if heated or struck.* A minute fragment of it placed on a glass plate, and touched with a red-hot wire, detonates loudly and shatters the glass like fulminate of silver. In a solution of hyposulphite of gold and sodium, acetylene gives a yellowish very explosive precipitate.

The copious formation of acetylene during the imperfect combustion of ether, is very readily shown by introducing a few drops of ether into a test-tube, adding a little ammoniacal solution of cuprous chloride, kindling the ether-vapour at the mouth of the tube, and inclining the latter so as to expose a large surface of the copper solution, when a large quantity of the red cuprous acetylide is produced. If nitrate of silver be substituted for the copper solution, the white precipitate of silver acetylide is formed abundantly.

Acetylene is a colourless gas having a peculiar odour, recalling that of the geranium, which is always perceived where coal gas is undergoing imperfect combustion. It burns with a very bright smoky flame. Its most remarkable property is that of inflaming spontaneously when brought in contact with chlorine. If a jet of the gas be allowed to pass into a bottle of chlorine, it will take fire and burn with a red flame, depositing much carbon. When chlorine is decanted up into a cylinder containing acetylene standing over water, a violent explosion immediately takes place, attended with a vivid flash, and separation of a large amount of carbon; $C_2H_2 + Cl_2 = C_2 + 2HCl$.

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* If the precipitate is prepared from a slightly ammoniacal solution of nitrate of silver, it is more sensitive to a blow.

When acetylene is passed into water, it is absorbed in sufficient quantity to impart a strong smell to the water, and to yield a decided precipitate with ammoniacal cuprous chloride and with silver nitrate.

If the acetylene copper precipitate be suspended in solution of ammonia, and heated with a little granulated zinc, the acetylene combines with the (*nascent*) hydrogen to form olefiant gas (C_2H_4). Further particulars respecting acetylene are given under *Organic Chemistry*.

73. ***Olefiant gas*** or ***ethylene*** (**$C_2H_4 = 28$ parts by weight = 2 volumes**).—This gas is found in larger quantity than acetylene, among the products of the action of heat upon coal and other substances rich in carbon, and it is an important constituent of the illuminating gases obtained from such materials.

Olefiant gas may readily be prepared by the action of strong sulphuric acid (oil of vitriol, H_2SO_4) upon alcohol (spirit of wine, C_2H_6O).

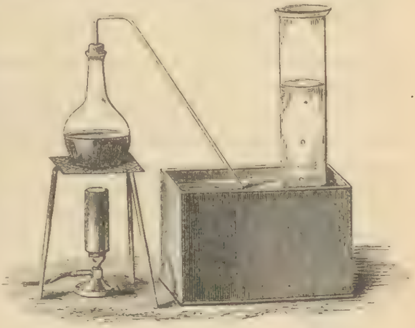

Fig. 90.—Preparation of olefiant gas.

Two measures of oil of vitriol are introduced into a flask (fig. 90), and one measure of alcohol is gradually poured in, the flask being agitated after each addition of the acid; much heat is evolved, and there would be danger in mixing large volumes suddenly.* On applying a moderate heat, the liquid will darken in colour, effervescence will take place, and the gas may be collected in jars filled with water. When the mixture has become thick, and the evolution of the gas is slow, the end of the tube must be removed from the water and the lamp extinguished. Three measured ounces of spirit of wine generally give about 500 cubic inches of olefiant gas (or 85 c.c. give 8 litres).

The gas will be found to have a very peculiar odour, in which that of ether and of sulphurous acid gas are perceptible. One of the jars may be closed with a glass plate, and placed upon the table with its mouth upwards; on the approach of a flame, the gas will take fire, burning with a bright white flame characteristic of olefiant gas, and seen to best advantage when, after kindling the gas, a stream of water is poured down into the jar in order to displace the gas (fig. 91).

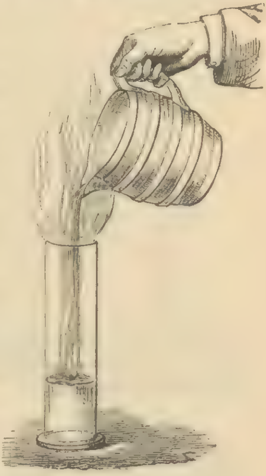

Fig. 91.

Another jar of the gas may be well washed by transferring it repeatedly from one jar to another under water, a little solution of potash may then be poured into it, and the jar violently shaken, its mouth being covered with a glass plate; the potash will remove all the sulphurous acid gas, and the gas will now exhibit the peculiar faint odour which belongs to olefiant gas.

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* If methylated spirit be employed, the mixture will have a dark red-brown colour.

The purified gas may be transferred, under water, to another jar, kindled and allowed to burn out; if a little lime-water be then shaken in the jar, its turbidity will indicate the presence of carbonic acid gas, which is produced together with water, when olefiant gas burns in air: $C_2H_4 + O_6 = 2CO_2 + 2H_2O$.

Ethylene has been liquefied by a pressure of 63 atmospheres at 10° C.*

On comparing the composition of olefiant gas (C_2H_4) with that of alcohol (C_2H_6O), it is evident that the former may be supposed to be produced from the latter by the abstraction of a molecule of water (H_2O) which is removed by the sulphuric acid, though other secondary changes take place, resulting in the separation of carbonaceous matter and the production of sulphurous acid gas. A more complete explanation of the action of sulphuric acid upon alcohol must be reserved for the chemical history of this compound.

Olefiant gas derives its name from its property of uniting with chlorine and bromine to form oily liquids, a circumstance which is applied for the determination of the proportion of this gas present in coal gas, upon which part of the illuminating value of coal gas depends. The compound with chlorine ($C_2H_4Cl_2$) is known as *Dutch liquid*, having been discovered by Dutch chemists, and is remarkable for its resemblance to chloroform in odour.

To exhibit the formation of Dutch liquid, a quart cylinder (fig. 92) is half filled with olefiant gas, and half with chlorine, which is rapidly passed up into it, from a bottle of the gas, under water. The cylinder is then closed with a glass plate, and supported with its mouth downwards under water in a *separating funnel* furnished with a glass stopcock. The volume of the mixed gases begins to diminish immediately, drops of oil being formed upon the side of the cylinder and the surface of the water. As the drops increase, they fall to the bottom of the funnel. Water must be poured into the funnel to replace that which rises into the cylinder, and when the whole of the gas has disappeared, the oil may be drawn out of the funnel through the stopcock into a test-tube, in which it is shaken with a little potash to absorb any excess of chlorine. The fragrant odour of the Dutch liquid will then be perceived, especially on pouring it out into a shallow dish.

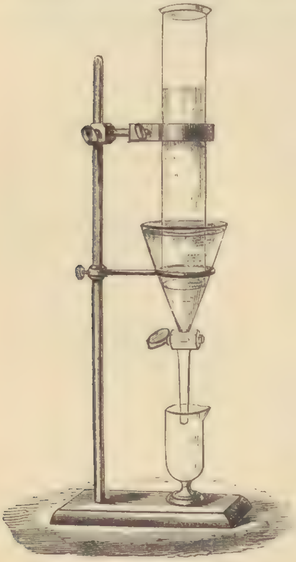

Fig. 92.

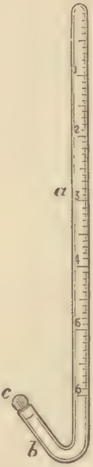

Fig. 93.

In applying this principle to the measurement of the illuminating hydrocarbons in coal gas, daylight must be excluded, or an error would be caused by the union of the free hydrogen with the chlorine or bromine. The *bromine test* may be applied in the tube represented in fig. 93. The gas to be examined is measured over water in the divided limb *a*, with due attention to temperature and pressure; the tube being held perpendicularly, the limb *b* will remain filled with water, so that gas cannot escape nor air enter. A drop or two of bromine is poured into this limb, which is then depressed beneath the water in the pneumatic trough, and closed by the stopper *c*. On shaking the gas with the water and bromine, the latter will absorb the illuminating hydrocarbons; and if the tube be again opened under water, the volume of the gas in *a* will be found to have diminished, and the diminution gives an approximate estimate of the olefiant gas and other illuminating hydrocarbons.

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* Liquid ethylene boils at − 102° C. By evaporating it in a vacuum, the temperature is reduced to − 136° C.

A very instructive experiment consists in filling a three-pint cylinder one-third full of olefiant gas, then rapidly filling it up, under water, with two pints of chlorine, closing its mouth with a glass plate, shaking it to mix the gases, slipping the plate aside and applying a light, when the mixture burns with a red flame which passes gradually down the cylinder, and is due to the combination of the hydrogen with the chlorine, the whole of the carbon being separated in the solid state—$C_2H_4 + Cl_4 = 4HCl + C_2$.

When olefiant gas is subjected to the action of high temperatures, as by passing through heated tubes, one portion is decomposed into marsh gas (CH_4) with separation of carbon, whilst another portion yields acetylene (C_2H_2) and hydrogen; these decompositions will be found to be of great importance in the manufacture of coal gas.

The action of heat upon olefiant gas is most conveniently shown by exposing it to the spark from an induction-coil.

The gas is confined in a tube (A, fig. 94) which is placed in a cylindrical jar (B) containing mercury. Through the mercury passes a copper wire (C) thrust through a glass tube (D) to insulate it from the mercury; this wire is connected with one of the wires (E) from the induction-coil, whilst the other (F) is allowed to dip into the mercury contained in the cylinder. On putting the coil in action (with two or three cells of Grove's battery), the spark will pass between the extremity (C) of the insulated copper wire and the surface of the mercury in the tube, decomposing the olefiant gas in its passage, and causing a separation of carbon, which sometimes forms a conducting communication, and allows the current to pass without a spark. This may be obviated by reversing the current, or by gently shaking the tube.

The olefiant gas will expand to nearly twice its former volume, so that the tube will gradually rise in the mercury, but the same distance may always be maintained for the passage of the spark.

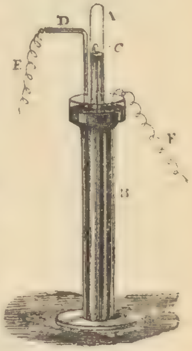

Fig. 94.

To show the production of acetylene, another arrangement will be found convenient (fig. 95). A globe with four necks is employed; through two of these necks are passed, air-tight with perforated corks, the copper wires connected with the induction-coil. A third neck receives a tube, conveying olefiant gas from a gasholder, whilst from the fourth proceeds a tube dipping to the bottom of a small cylinder. When the whole of the air has been displaced by olefiant gas, a solution of cuprous chloride in ammonia is poured into the cylinder, and the gas allowed to bubble through it, when the absence of acetylene will be shown by there being no red compound formed. As soon, however, as the spark is passed, the red precipitate will appear, and, in a very few minutes, a large quantity will be deposited. Coal gas may be employed instead of olefiant gas, but of course less of the copper compound will be obtained.

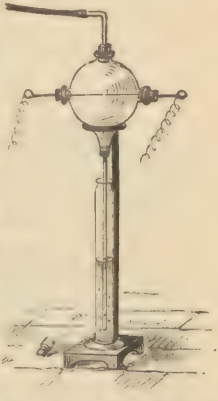

Fig. 95.—Preparation of cuprous acetylide from olefiant gas.

74. *Marsh gas* or *light carburetted hydrogen* ($CH_4 = 16$ parts by weight $= 2$ volumes).—This hydrocarbon is found in nature, being produced wherever vegetable matter is undergoing decomposition in the presence of moisture. The bubbles rising from stagnant pools, when collected and examined, are found to contain marsh gas mixed

with carbonic acid gas, and there is reason to believe that these two gases represent the principal forms in which the hydrogen and oxygen respectively were separated from wood during the process of its conversion into coal. This would account for the constant presence of this gas in the coal formations, where it is usually termed *fire-damp.* It is occasionally found pent up under pressure between the layers of coal, and the pores of the latter are sometimes so full of it that it may be seen rising in bubbles when the freshly hewn coal is thrown into water. Perhaps a similar origin is to be ascribed to the liquid hydrocarbons chemically similar to marsh gas, which are found so abundantly in Pennsylvania and Canada, and are known by the general name of *petroleum.* From certain gas-springs in Pennsylvania, marsh gas, olefiant gas, and ethyle hydride, C_2H_6, are discharged at very high pressure, and are employed for heating and lighting.

Marsh gas is obtained artificially by the following process :—

500 grains of dried sodium acetate are finely powdered and mixed, in a mortar, with 200 grains of solid potash, and 300 grains of powdered quicklime (or with 500 grains of the mixture of calcium hydrate and sodium hydrate, which is sold as *soda-lime*). The mixture is heated in a Florence flask (or better a copper tube, for the alkali corrodes the glass) and the gas collected over water (fig. 96).

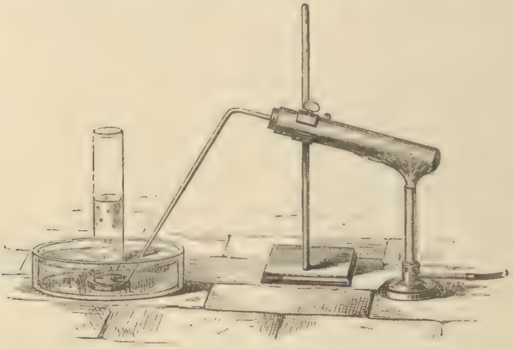

Fig. 96.—Preparation of marsh gas.

The decomposition will be evident from the following equation :—

$$\underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + CH_4.$$

The marsh gas will be easily recognised by its burning with a pale illuminating flame, far inferior in brilliancy to those of olefiant gas and acetylene, but unattended with smoke.*

The properties of this gas deserve a careful study, on account of the frequent fatal explosions to which it gives rise in coal-mines, where it is often found accumulated under pressure, and discharging itself with considerable force from the fissures or *blowers* made in hewing the coal. Marsh gas has no characteristic smell like coal gas, and the miner thence receives no timely warning of its presence ; it is much lighter than air (sp. gr. 0.5596), and therefore very readily diffuses† itself

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* The gas prepared by the above process contains acetone, which increases its luminosity. For the preparation of pure marsh gas, see *Organic Chemistry*.

† *Ansell's fire-damp indicator* is an apparatus in which the high rate of diffusion of marsh gas is taken advantage of in order to detect its presence in the air of mines. The apparatus represented in fig. 14 illustrates its principle.

(page 20) through the air of the mine, with which it forms an explosive mixture as soon as it amounts to one-eighteenth of the volume of the air. The gas issuing from the blower would burn quietly on the application of a light, since the marsh gas is not explosive unless mixed with the air, when a large volume of the gas is burnt in an instant, causing a sudden evolution of a great deal of heat, and a consequent sudden expansion or explosion exerting great mechanical force. The most violent explosion takes place when 1 volume of marsh gas is mixed with 2 volumes of oxygen, since this quantity is exactly sufficient to effect the complete combustion of the carbon and hydrogen of the gas, and therefore to evolve the greatest amount of heat: $CH_4 + O_4 = CO_2 + 2H_2O$. The calculated pressure exerted by the exploding mixture of marsh gas and oxygen amounts to 37 atmospheres, or 555 lbs. upon the square inch. Since air contains one-fifth of its volume of oxygen, it would be necessary to employ 10 volumes of air to 1 volume of marsh gas in order to obtain perfect combustion, but the explosion will be much less violent on account of the presence of the 8 volumes of inert nitrogen, the calculated pressure exerted by the explosion being only 14 atmospheres, or 210 lbs. on the square inch. Of course, if more air is employed, the explosion will be proportionally weaker, until, when there are more than 18 volumes of air to each volume of marsh gas, the mixture will be no longer explosive, but will burn with a pale flame around a taper immersed in it. The carbonic acid gas resulting from the explosion is called by miners the *after-damp*, and its effects are generally fatal to those who may have escaped death from the explosion itself.

Coal gas, which contains much hydrogen, requires a smaller volume of air than marsh gas to render it explosive. With 16-candle gas, such as is used in London, 6 vols. of air to 1 vol. of gas would give the most powerful explosion.

Fortunately, marsh gas requires a much higher temperature to inflame it than most other inflammable gases; a solid body at an ordinary red heat does not kindle the gas unless kept in contact with it for a considerable period; contact with flame, or with a body heated to whiteness, being required to ignite it instantaneously.

If two strong gas cylinders be filled, respectively, with mixtures of 2 volumes hydrogen with 1 volume oxygen, and of 1 volume marsh gas and 2 volumes oxygen, it will be found, on holding them with their mouths downwards, and inserting a red-hot iron bar (fig. 97), that the marsh gas mixture will not explode, but if the bar be transferred at once to the hydrogen mixture, explosion will take place. A lighted taper may then be used to explode the marsh gas and oxygen.

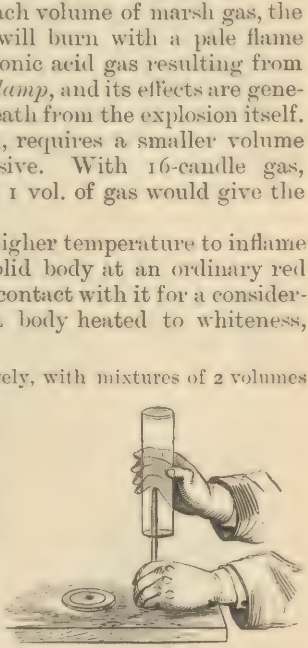

Fig. 97.

In consequence of the high temperature required to inflame the mixture of marsh gas and air, it is necessary that the mixture be allowed to remain for an appreciable time in contact with the flame before its particles are raised to the igniting point. It was on this principle that Stephenson's original safety lamp was constructed, the flame being surrounded with a tall glass chimney, the rapid draught through which caused the explosive mixture to be hurried past the flame without igniting.

To illustrate this, a copper funnel holding about two quarts (fig. 98) is employed, the neck of which has an opening of about ¼ inch in diameter. The funnel being placed mouth downwards in the pneumatic trough, the orifice is closed with the finger, and a half-pint of coal gas passed up into the funnel. The latter is now raised from the water, so that it may become entirely filled with air. By depressing the funnel to a considerable depth in the water, the aperture being still closed by the finger, the mixture will be confined under considerable pressure, and if a lighted taper be held to the aperture, and the finger removed, it will be found that the mixture sweeps past the flame without exploding, until the water has reached the same level in the funnel as in the trough, when the gas comes to rest and explodes with great violence.

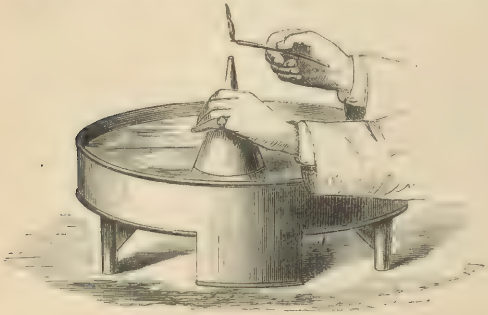

Fig. 98.

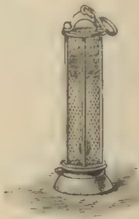

Fig. 99.

Davy's safety lamp (fig. 99) is an application of the principle that ignited gas (*flame*) is extinguished by contact with a large surface of a good conductor of heat, such as copper or iron.

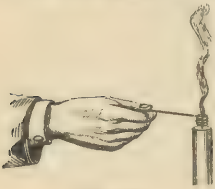

Fig. 100.

If a thin copper wire be coiled round into a helix, and carefully placed over the wick of a burning taper (fig. 100), the flame will be at once extinguished, its heat being so rapidly transmitted along the wire that the temperature falls below the point at which the combustible gases enter into combination with oxygen, and therefore the combustion ceases. If the coil be heated to redness in a spirit-lamp flame before placing it over the wick, it will not abstract the heat so readily, and will not extinguish the flame. If a copper tube were substituted for the coiled wire, the same result would be obtained, and by employing a number of tubes of very small diameter, so that the metallic surface may be very large in proportion to the volume of ignited gas, the most energetic combustion may be arrested, as in the case of *Hemming's safety jet*, which consists of a brass tube tightly stuffed with thin copper wires so as to leave very narrow passages, thus rendering it impossible for the oxyhydrogen flame at the jet to pass back and ignite the mixture in the reservoir. It is evident that the exposure of a large extent of cooling surface to the action of the flame may be effected either by increasing the length or by diminishing the width of the metallic tubes, so that wire gauze, which may be regarded as a collection of very short tubes, will form an effectual barrier to flame, provided that it has a sufficient number of meshes to the inch.

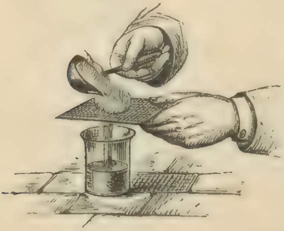

Fig. 101.

If a piece of iron wire gauze, containing about 400 meshes to the square inch, be depressed upon a flame, it will extinguish that portion with which it is in contact, and the combustible gas which escapes through the gauze may be kindled by a lighted match held on the upper side. By holding the gauze 2 or 3 inches above a gas jet, the gas may be lighted above it without communicating the flame to the burner itself.

When blazing spirit is poured upon a piece of wire gauze (fig. 101), the flame will remain upon the gauze, and the extinguished spirit will pass through. A little benzene or turpentine may be added to the spirit, so that its flame may be more visible at a distance.

The safety lamp (fig. 99) is an oil lamp, the flame of which is surrounded by a cage of iron wire gauze, having 700 or 800 meshes in the square inch, and made double at the top where the heat of the flame chiefly plays. This cage is protected by stout iron wires attached to a ring for suspending the lamp. A brass tube passes up through the oil reservoir, and in this there slides, with considerable friction, a wire bent at the top, so that the wick may be trimmed without taking off the cage.

If this lamp be suspended in a large jar, closed at the top with a perforated wooden cover A (fig. 102), and having an aperture (B) below, through which coal gas is allowed to pass slowly into the jar, the flame will be seen to waver, to elongate itself very considerably, and will be ultimately extinguished, when the wire cage will be seen to be filled with a mixture of coal gas and air burning tranquilly within the gauze, which prevents the flame from passing to ignite the explosive atmosphere surrounding the lamp; that an explosive mixture really fills the jar may be readily ascertained by introducing, through an aperture (C) in the cover, the unprotected flame of a taper, when an explosion will take place.

This experiment illustrates the action of the Davy lamp in a mine which contains fire-damp. It would obviously be unsafe to allow the lamp to remain in the explosive mixture when the cage is filled with flame, for the gauze would either become sufficiently heated to kindle the surrounding gas, or would be oxidised and eaten into holes, which would allow the passage of the flame. Nor should the lamp be exposed to a very strong current, which might possibly be able to carry the flame through the meshes.

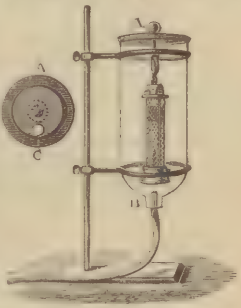

Fig. 102.

The great defect of the Davy lamp is that it does not afford sufficient light, and it has been modified so as partially to remove this defect, by substituting glass or talc for some portions of the wire gauze. It is now usual, however, to employ the Davy lamp merely in order to test the state of the air in the different parts of the mine. All coal contains a considerable quantity of gas *occluded* or condensed in its pores, part of which issues when the surface of the coal is exposed, and part is retained, and can be extracted by exposure in vacuo and moderately heating. Bituminous coals evolve more CO_2 and N, and less CH_4, than steam coal and anthracite. Hence bituminous coals may often be worked with naked lights, while seams of steam coal and anthracite are dangerous. Cannel coal has occluded, beside the above gases, some *ethane*, C_2H_6, and Whitby jet has been found to contain *butane*, C_4H_{10}. The gas from *blowers* sometimes contains 97 per cent. by volume of marsh gas, with a little CO_2 and N. Whenever naked flames are used in the mine, there must always be great risk; in most seams of coal there are considerable accumulations of fire-damp; when a fissure is made, the gas escapes very rapidly from the *blower*, and the air in its vicinity may soon become converted into an explosive mixture. In mines where small quantities of fire-damp are known to be continually escaping from the coal, ventilation is depended upon in order to dilute the gas with so large a volume of air that it is no longer explosive, and finally to sweep it out of the mine; but it has occasionally happened that the ventilation has been interfered with by a door having been left open in one of the galleries, or by a passage having been obstructed through the accidental falling in of a portion of the coal, and an explosive mixture has then been formed.

Galloway has shown that the presence of fine dust of coal in the air of the mine greatly increases the liability to explosion. Most combustible substances mixed in a finely divided state with air, burn so rapidly as to produce effects of explosion. Flour mills have been destroyed from this cause in very dry weather.

If some *lycopodium* be placed in a glass funnel, the stem of which has been lightly stopped with wool, and has two or three feet of wide vulcanised tubing attached to it, the lycopodium may be blown out in a cloud by a sudden puff of air, and if a lighted taper be held in the cloud, an immense volume of flame will be formed.

(Lycopodium is the seed of the club moss,—*Lycopodium clavatum*,—and is used for theatrical lightning. It is sometimes called *vegetable brimstone*.)

An ingenious fire-damp indicator has been constructed of two platinum wires, which are heated by a magneto-electric current. One wire is sheltered from the fire-damp, and the other, being exposed to it, glows more strongly on account of the slow combustion of the fire-damp at the surface of the platinum (see *Platinum*). By a careful comparison of the two wires, it is said that .25 per cent. of marsh gas in air may be detected, whilst the Davy lamp will not indicate less than 2 per cent.

Structure of Flame.

75. The consideration of the structure and properties of ordinary flames is necessarily connected with the history of olefiant gas and marsh gas. Flame may be defined as gaseous matter heated to the temperature at which it becomes visible, or emits light. Solid particles begin, for the most part, to emit light when heated to about 1000° F.; but gases, on account of their lower radiating power, must be raised to a far higher temperature, and hence the point of visibility is seldom attained, except by gases which are themselves combustible, and therefore capable of producing, by their own combination with atmospheric oxygen, the requisite degree of heat. The presence of a combustible gas (or vapour), therefore, is one of the conditions of the existence of flame; a diamond, or a piece of thoroughly carbonised charcoal, will burn in oxygen with a steady glow, but without flame, since the carbon is not capable of conversion into vapour, while sulphur burns with a voluminous flame, in consequence of the facility with which it assumes the vaporous condition. It will be observed, moreover, that in the case of a non-volatile combustible, the combination with oxygen is confined to the surface of contact, whilst in the flame of a gas or vapour the combustion extends to a considerable depth, the oxygen intermingling with the gaseous fuel.

Flames may be conveniently spoken of as *simple* or *compound*, accordingly as they involve one or more phenomena of combustion; thus, for example, the flames of hydrogen and carbonic oxide are simple, whilst those of marsh gas and olefiant gas are compound, since they involve both the conversion of hydrogen into water and of carbon into carbon dioxide.

It is obvious that simple flames must be hollow in ordinary cases, such as that of a gas issuing from a tube into the air, the hollow being occupied by the combustible gas to which the oxygen does not penetrate.

All the flames which are ordinarily turned to useful account are compound flames, and involve several distinct phenomena. Before examining these more particularly, it will be advantageous to point out the conditions which regulate the luminosity of flames.

In order that a flame may emit a brilliant light, it is essential that it should contain particles which, either from their own nature, or from the conditions under which they are placed, do not admit of indefinite expansion by the heat of the flame, but are capable of being heated to *incandescence*. Thus the flame of the oxyhydrogen blowpipe (p. 41) emits a very pale light, but if the mixture of oxygen and hydrogen be restrained from expanding when fired, as in the Cavendish eudiometer (p. 36), it gives a bright flash; or if the flame be directed upon some solid body little affected by the heat, such as lime, the light is very intense.

Phosphorus and arsenic burn with very luminous flames, in consequence of the formation of very dense vapours of phosphoric and arsenious oxides during the combustion; the density of the vapours being here attended with the same result as that produced by the restrained expansion of the steam formed in the Cavendish eudiometer.

It is not necessary that the incandescent matter should be a product of the combustion; any extraneous solid in a finely divided state will confer illuminating power upon a flame. Thus the flame of hydrogen may be rendered highly luminous by blowing a little very fine charcoal powder into it, from the bottle represented in fig. 103.

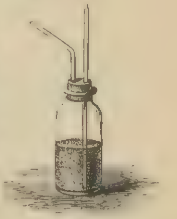
Fig. 103.

The luminosity of all ordinary flames is due to the presence of highly heated carbon in a state of very minute division, and it remains to consider the changes by which this finely divided carbon is separated in the flame.

A candle, a lamp, and a gas burner, exhibit contrivances for procuring light artificially in different degrees of complexity, the candle being the most complex of the three. When a new candle is lighted, the first portion of the wick is burnt away until the heat reaches that part which is saturated with the wax or tallow of which the candle is composed; this wax or tallow then undergoes destructive distillation, yielding a variety of products, among which olefiant gas is found in abundance. The flame furnished by the combustion of these products melts the fuel around the base of the wick, through which it then mounts by capillary attraction, to be decomposed in its turn, and to furnish fresh gases for the maintenance of the flame. In a lamp, the fuel being liquid at the commencement, the process of fusion is dispensed with; and in a gas burner, where the fuel is supplied in a gaseous form, the process of destructive distillation has been already carried on at a distance. It will be seen, however, that the final result is similar in all three cases, the flame being maintained by such gases as acetylene, marsh gas, and olefiant gas arising from the destructive distillation of wax, tallow, oil, coal, &c.

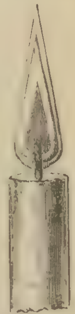
Fig. 104.

On examining an ordinary flame, that of a candle, for instance, it is seen to consist of three concentric cones (fig. 104), the innermost around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be scarcely visible in broad daylight.

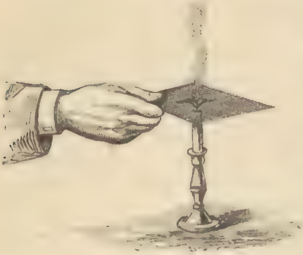

Fig. 105.

The dark innermost cone consists merely of the gaseous combustible to which the air does not penetrate, and which therefore is not in a state of combustion.

The nature of this cone is easily shown by experiment: a strip of cardboard held across the flame near its base will not burn in the centre where it traverses the innermost cone; a piece of wire gauze depressed upon the flame near the wick (fig. 105) will allow the passage of the combustible gas, which may be kindled above it. The gas may be conveyed out of the flame by means of a glass tube, inserted into the innermost cone, and may be kindled at the other extremity of the tube, which should be inclined downwards (fig. 106).

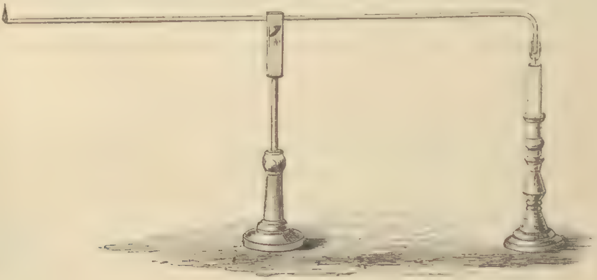

Fig. 106.

A piece of phosphorus in a small spoon held in the interior of the flame of a spirit-lamp will melt and boil, but will not burn unless it be removed from the flame, and may then be extinguished by replacing it in the flame.

The combustible gas from the interior of a flame may be collected in a flask (fig. 107) furnished with two tubes, one of which (A) is drawn out to a point for insertion into the flame, whilst the other (B), which passes to the bottom of the flask, is bent over and prolonged by a piece of vulcanised tubing so that it may act as a siphon. The flask is filled up with water, the jet inserted into the interior of a flame, and the siphon set running by exhausting it with the mouth. As the water flows out through the siphon, the gas is drawn into the flask, and after removing the tube from the flame, the gas may be expelled by blowing down the siphon tube, and may be burnt at the jet. When a candle is used for this experiment, some solid products of destructive distillation will be found condensed in the flask.

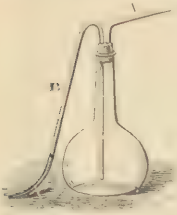

Fig. 107.

In the second or luminous cone, combustion is taking place, but it is by no means perfect, being attended by the separation of a quantity of carbon, which confers luminosity upon this part of the flame. The presence of free carbon is shown by depressing a piece of porcelain upon this cone, when a black film of soot is deposited. The liberation of the carbon is due to the decomposition of the olefiant gas and similar hydrocarbons by the heat, which separates the carbon from the hydrogen, and this latter undergoing combustion evolves sufficient heat to raise the separated carbon to a white heat, the supply of air which penetrates into this portion of the flame being insufficient to effect the combustion of the whole of the carbon.

Some very simple experiments will illustrate the nature of the luminous portion of flame.

Over an ordinary candle flame (fig. 108) a tube may be adjusted so as to convey the finely divided carbon from the luminous part of the flame into the flame of hydrogen, which will thus be rendered as luminous as the candle flame, the dark colour of the carbon being apparent in its passage through the tube.

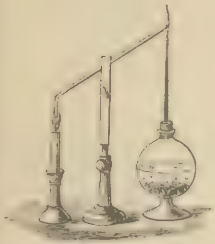
Fig. 108.

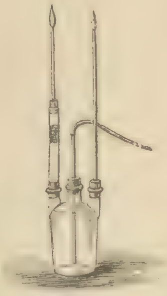
Fig. 109.

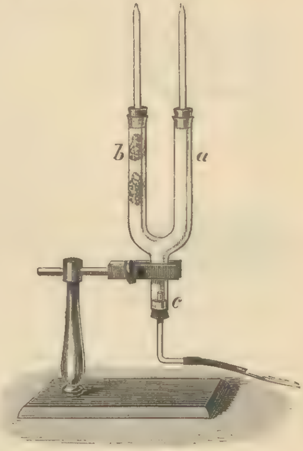

Fig. 110.

A bottle furnished with two straight tubes (fig. 109) is connected with a reservoir of hydrogen. One of the tubes is provided with a small piece of wider tube containing a tuft of cotton wool. On kindling the gas at the orifice of each tube, no difference will be seen in the flames until a drop of benzene (C_6H_6) is placed upon the cotton, when its vapour, mingling with the hydrogen, will furnish enough carbon to render the flame brilliantly luminous.

Fig. 110 shows a more convenient apparatus for the same purpose; the hydrogen being passed in through *c*, burns from the tube *a* with non-luminous flame, and from the tube *b*, after passing over a piece of cotton moistened with benzene, with a luminous flame.

The pale outermost cone, or *mantle*, of the flame, in which the separated carbon is finally consumed, may be termed the cone of perfect combustion, and is much thinner than the luminous cone, the supply of air to this external shell of flame being unlimited, and the combustion therefore speedily effected.

The mantle of the flame may be rendered more visible by burning a little sodium near the flame, when the mantle is tinged strongly yellow.

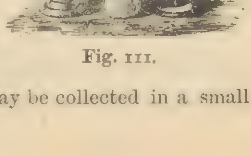
Fig. 111.

By means of a siphon about one-third of an inch in diameter (fig. 111), the nature of the different portions of an ordinary candle flame may be very elegantly shown. If the orifice of the siphon be brought just over the extremity of the wick, the combustible gases and vapours will pass through it, and may be collected in a small flask, where they can be kindled by a taper. On raising the orifice into the luminous portion of the flame, voluminous clouds of black smoke will pour over into the flask, and if the siphon be now raised a little above the point of the flame, carbonic acid gas can be collected in the flask, and may be recognised by shaking with lime-water.

The reciprocal nature of the relation between the combustible gas and the air which supports its combustion, may be illustrated in a striking manner by burning a jet of air in an atmosphere of coal gas.

A quart glass globe with three necks is connected at A (fig. 112) with the gas-pipe by a vulcanised tube. The second neck (B), at the upper part of the globe, is connected by a short piece of vulcanised tube with a piece of glass tube about $\frac{1}{2}$ inch wide, from which the gas may be burnt. Into the third and lowermost neck is inserted, by means of a cork, a thin brass tube C (an old cork-borer), about $\frac{1}{3}$ inch in diameter. When the gas is turned on, it may be lighted at the upper neck; and if a lighted match be then quickly thrust up the tube C, the air which enters it will take fire, and burn inside the globe.

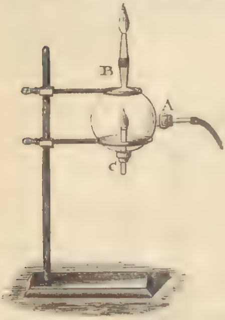

Fig. 112.—Air burning in coal gas.

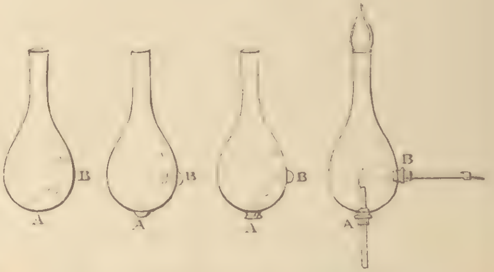

Fig. 113.—To make a three-necked flask.

A very inexpensive apparatus for this purpose may be constructed from a common Florence oil-flask. By applying a blowpipe flame at A (fig. 113), so as to heat to whiteness a spot as large as a threepenny-piece, and quickly blowing into the neck of the flask, the heated portion of the glass may be made to bulge out. A similar protuberance is then to be formed at B. A sharp-pointed flame is directed upon A, and the glass burst by blowing into the flask whilst it is still exposed to the flame. By fusing the edges of the hole thus produced, and turning them outwards with the end of a file, a short neck may be formed capable of receiving a cork. When this is cool, it is closed with a cork, and a second similar neck is produced at B.

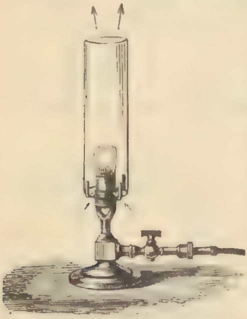

Fig. 114.—Argand burner.

A simple experiment to show the burning of gas in air may be made with an Argand burner (fig. 114). The flame having been turned low, a dish (or dial-glass containing water to prevent cracking) is placed so as to close the top of the chimney, when the gas flame will be extinguished, and the air which enters the inner circle will burn with a pale flame which may be made more visible by thrusting up a copper wire dipped in hydrochloric acid. A bottomless beaker makes a good chimney for this purpose.

From this review of the structure of flame, it is evident that, in order to secure a flame which shall be useful for illumination, attention must be paid to the supply of oxygen (or air), and to the composition of the fuel employed. The use of the chimney of an Argand burner (fig. 114) affords an instance of the necessity for attention to the proper supply of air.

Without the chimney, the flame is red at the edges, and smoky, for the supply of air is not sufficient to consume the whole of the carbon which is separated, and the temperature is not competent to raise it to a bright white heat, defects which are remedied as soon as the chimney is placed over it and the rapidly ascending heated column of air draws in a liberal supply beneath the burner, as indicated by the arrows.

By using two chimneys, and causing the air to pass down between them, so as to be heated to about 500° F. before reaching the flame, an equal amount of light may be obtained from a much smaller supply of gas.

The smokeless gas burners employed in laboratories and kitchens exhibit the result of mixing the gas with a considerable proportion of air before burning it, the luminous part of the flame then entirely disappearing, with great augmentation of the temperature of the flame, since the carbon is burnt simultaneously with the hydrogen, and the size of the flame is diminished.

The most efficient burner of this kind (*Bunsen's burner*, fig. 115) is that in which the gas is conveyed through a narrow jet into a wide tube, at the base of which there are four large holes for the admission of air. When a good supply of gas is turned on, a quantity of air, about twice the volume of the gas, is drawn in through the lower apertures, and the mixture of air and gas may be kindled at the orifice of the wide tube, its rapid motion preventing the flame from passing down within the tube. This tube is sometimes surmounted by a rosette burner to distribute the flame. By closing the air-holes with the fingers, a luminous flame is at once produced.

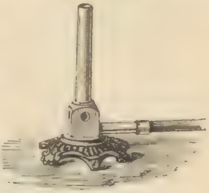

Fig. 115.—Bunsen's burner.

The luminosity of the flame may also be destroyed by supplying nitrogen instead of air to the Bunsen burner, when the diminution of light is due partly to the increased area of the flame and partly to the cooling effect of the nitrogen.

The temperature of the Bunsen flame is estimated to be 1200° C. in the inner blue flame, and 1350° C. in the outer layer or mantle of the flame.

The *gauze burner* (fig. 116) consists of an open cylinder surmounted by wire gauze. When this is placed over the gas burner, a supply of air is drawn in at the bottom by the ascending stream of gas, and the mixture burns above the gauze with a very hot smokeless flame, the metallic meshes preventing the flame from passing down to the gas below.

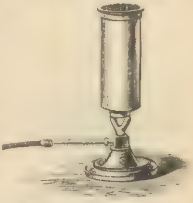

Fig. 116.—Gauze burner.

The luminosity of a flame is materially affected by the pressure of the atmosphere in which it burns, a diminution of pressure causing a loss of illuminating power. If the light of a given flame burning in the air when the barometer stands at 30 inches be represented by 100, each diminution of one inch in the height of the barometer will reduce the luminosity by five; and conversely, when the barometer rises one inch, the luminosity will be increased by five. This is not due to any difference in the rate of burning, which remains pretty constant, but to the more complete interpenetration of the rarefied air and the gases composing the flame; this gives rise to the separation of a smaller quantity of incandescent carbon. In air at a pressure of 120 inches of mercury, the flame of alcohol is highly luminous.

The following table exhibits the composition of some of the principal substances concerned in producing ordinary flames:—

Fuel.	Formula.	Weight of Carbon	
		in One Volume of Vapour.	in Proportion to Hydrogen.
Marsh gas	CH_4	6	3
Olefiant gas	C_2H_4	12	6
Acetylene	C_2H_2	12	12
Alcohol	C_2H_6O	12	4
Benzene	C_6H_6	36	12
Paraffin oil	C_7H_{16}	42	5·3
Turpentine	$C_{10}H_{16}$	60	7·5
Naphthalene	$C_{10}H_8$	60	15
Paraffin wax	$C_{16}H_{34}$	96	5.6
Wax	$C_{46}H_{92}O_2$	...	6
Stearin (tallow)	$C_{57}H_{110}O_6$	...	6.2
Olein (oil)	$C_{57}H_{104}O_6$	...	6.6

It will be observed that marsh gas and alcohol have no illuminating value, because they contain too little carbon in proportion to the hydrogen. On the other hand, acetylene, benzene, naphthalene, and turpentine contain too much carbon, and burn with smoky flames. Paraffin oil, though containing less carbon in proportion to hydrogen than the animal and vegetable oils (olein), gives a flame with more tendency to smoke, because of the large amount of carbon in one volume of its vapour. The animal and vegetable oils are decomposed by the heat into simpler molecules, such as marsh gas, olefiant gas, and acetylene, which contain less carbon in each volume of vapour. Benzene (coal naphtha) vapour when mixed with air burns with a smokeless flame.

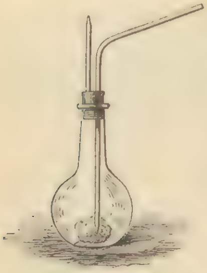
Fig. 117.

If a piece of cotton wool, moistened with benzene, be placed in a flask provided with two tubes (fig. 117), it will be found, on gently warming the flask by dipping it into hot water, and blowing through one of the tubes, that the mixture of benzene vapour and air issuing from the other tube will burn with a smokeless bright flame.

If coal gas, which is essentially a mixture of hydrogen, marsh gas, and olefiant gas, and generally contains rather too much hydrogen in proportion to its carbon, be enriched with carbon by passing over benzene (light coal naphtha) or naphthalene, as in the *albo-carbon light*, it burns with a far more luminous flame.

76. *The blowpipe flame.*—The principles already laid down will render the structure of the blowpipe flame easily intelligible. It must be remembered that in using the blowpipe, the stream of air is not propelled from the lungs of the operator (where a great part of its oxygen would have been consumed), but simply from the mouth, by the action of the muscles of the cheeks. The first apparent effect upon the flame is entirely to destroy its luminosity, the free supply of air effecting the immediate combustion of the carbon. The size of the flame, moreover, is much diminished, and the combustion being concentrated into a smaller space, the temperature must be much higher at any given point of the flame. In structure, the blowpipe flame is similar to the ordinary flame, consisting of three distinct cones, the innermost of which (A, fig. 118) is filled with the cool mixture of air and combustible gas. The

second cone, especially at its point (R), is termed the *reducing* flame, for the supply of oxygen at that part is not sufficient to convert the carbon into carbon dioxide, but leaves it as carbonic oxide, which speedily reduces almost all metallic oxides placed in that part of the flame to the metallic state. The outermost cone (O) is called the *oxidising* flame, for there the supply of oxygen from the surrounding air is unlimited, and any substance prone to combine with oxygen at a high temperature is oxidised when exposed to the action of that portion of the flame; the hottest point of the blowpipe flame, where neither fuel nor oxygen is in excess, appears to be a very little in advance of the extremity of the second (reducing) cone. The difference in the operation of the two flames is readily shown by placing a little red lead (oxide of lead) in a shallow cavity scooped upon the surface of a piece of charcoal (fig. 119), and directing the flames upon it in succession; the inner flame will reduce a globule of metallic lead, which may be reconverted into oxide by exposing it to the outer flame.*

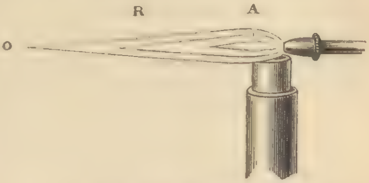

Fig. 118.—Blowpipe flame.

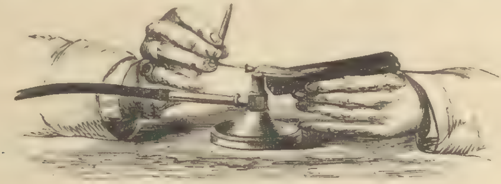

Fig. 119.—Reduction of metals on charcoal.

The immense service rendered by this instrument to the chemist and mineralogist is well known.

By forcing a stream of oxygen through a flame, from a gas-holder or bag, an intensely hot blowpipe flame is obtained, in which pipeclay and platinum may be melted, and iron burns with great brilliancy.

Fletcher's *hot-blast blowpipe* (fig. 120) produces a much higher temperature than the ordinary blowpipe. Coal gas is supplied through the tube *g*, and is kindled at the Bunsen burners *b b* and at the orifice *f*, the supply to the former being regulated by the stop-cock *c*, and to the latter by the stop-cock *d*. The flames of the Bunsen burners heat the spiral copper tube *e* to redness, so that the air blown in through the flexible tube *a* is strongly heated before being projected into the flame through a blowpipe jet at *f*. Thin platinum wires melt easily in this flame, and thin iron wires burn away rapidly.

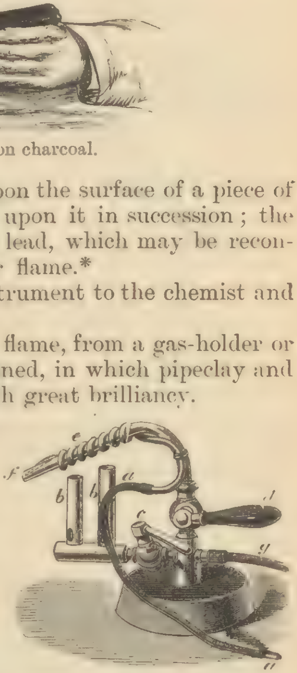

Fig. 120.—Hot-blast blowpipe.

77. *Determination of the composition of gases containing carbon and hydrogen.*—In order to ascertain the pro-

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* By directing the reducing flame upon the metallic oxide in the cavity, and allowing the oxidising flame to sweep over the surface of the charcoal, as shown in the figure, a yellow *incrustation* of oxide of lead is formed upon the surface of the charcoal, which affords additional evidence of the nature of the metal.

portions of carbon and hydrogen present in a gas, a measured volume of the gas is mixed with an excess of oxygen, the volume of the mixture carefully noted, and explosion determined by passing the electric spark; the gas remaining after the explosion is measured and shaken with potash, which absorbs the carbonic acid gas, from the volume of which the proportion of carbon may be calculated. For example,

0.4 cubic inch of marsh gas, mixed with
1.0 ,, oxygen, and exploded, left
0.6 ,, gas; shaken with potash, it left
0.2 ,, oxygen,

showing that 0.4 cubic inch of carbonic acid gas had been produced. This quantity would contain 0.4 cubic inch of oxygen. Deducting this last from the total amount of oxygen consumed (0.8 cubic inch), we have 0.4 cubic inch for the volume of oxygen consumed by the hydrogen. Now, 0.4 cubic inch of oxygen would combine with 0.8 cubic inch of hydrogen, which represents therefore the amount of hydrogen in the marsh gas employed. It has thus been ascertained that the marsh gas contains twice its volume of hydrogen.

Sp. gr. (to H) or weight of 1 volume of marsh gas . .	= 8
weight of 2 volumes (one molecule) . .	= 16
2 volumes of marsh gas contain 4 volumes H, weighing .	4
2 volumes of marsh gas contain x volume C, weighing . .	12

For the purpose of illustration, the analysis of marsh gas may be effected in a Ure's eudiometer (fig. 121), but a considerable excess of oxygen should be added to moderate the explosion. The eudiometer having been filled with water, 0.1 cubic inch of marsh gas is introduced into it, as described at p. 38, and having been transferred to the closed limb and accurately measured after equalising the level of the water, the open limb is again filled up with water, the eudiometer inverted in the trough, and 1.2 cubic inch of oxygen added; this is also transferred to the closed limb and carefully measured. The electric spark is passed through the mixture (see p. 38), the open limb being closed by the thumb. The level of the water in both limbs is then equalised, and the volume of gas measured. The open limb is filled up with a strong solution of potash, and closed by the thumb, so that the gas may be transferred from the closed to the open limb and back, until its volume is no longer diminished by the absorption of carbon dioxide. The volume of residual oxygen having been measured, the calculation is effected as above described.

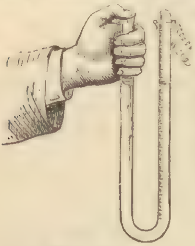

Fig. 121.
Siphon eudiometer.

The results are more exact when the eudiometer is filled with mercury instead of water.

Coal Gas.

78. The manufacture of coal gas is one of the most important applications of the principle of destructive distillation, and affords an excellent example of the tendency of this process to develop new arrangements of the elements of a compound body. The action of heat upon coal, in a vessel from which air is excluded, gives rise to the production of a very large number of compounds containing some two or more of the five elements of the coal, in different proportions, or in different forms of arrangement. Although no clue has yet been obtained to indicate the true arrangement of these elements in the original coal (or, as it is termed, the *constitution* of the coal), it is certain that these various

compounds do not exist in it before the application of heat, but are really the results of its action; that they are indeed *products* and not *educts*.

The most important forms assumed by the carbon and hydrogen when coal is strongly heated, are—

Gases	Hydrogen	
	Marsh gas	CH_4
	Olefiant gas	C_2H_4
	Acetylene	C_2H_2
	Butylene	C_4H_8
Liquids	Benzene	C_6H_6
	Toluene	C_7H_8
Solids.	Naphthalene	$C_{10}H_8$
	Anthracene	$C_{14}H_{10}$
	Paraffin	$C_{16}H_{34}$
	Coke	C

The nitrogen of the coal reappears in the forms of—

Gases	Nitrogen		
	Ammonia	NH_3	Alkaline
Liquids	Aniline	C_6H_7N	
	Quinoline	C_9H_7N	
	Hydrocyanic acid	CHN	

The oxygen contributes to the production of—

Gases	Carbonic oxide	CO
	Carbon dioxide	CO_2
Liquids	Water	H_2O
	Acetic acid	$C_2H_4O_2$
	Carbolic acid	C_6H_6O

Sulphur is found among the products as—

Sulphuretted hydrogen *gas*	H_2S
Liquid (very volatile) Carbon disulphide	CS_2

The illuminating gas obtained from coal consists essentially of free hydrogen, marsh gas, olefiant gas, and carbonic oxide, with small quantities of acetylene, benzene vapour, and some other substances. Its specific gravity is about 0.4, and varies inversely as its illuminating value.

A fair general idea of its composition is given by the following table :—

Composition by volume.	*Gas from Newcastle Coal.*	*Gas from Cannel.*
Hydrogen	43.99	41.72
Marsh gas	39.36	41.88
Carbonic oxide	6.42	4.98
Olefiant gas*	4.12	8.72
Carbonic acid gas	Traces	0.00
Nitrogen	5.40	2.71
Oxygen	0.40	0.00
	99.69	100.01

The only constituents which contribute directly to the illuminating value of the gas are the vapour of benzene, acetylene, olefiant gas, and similar hydrocarbons.

The most objectionable constituent is the sulphur present as sulphuretted hydrogen and bisulphide of carbon, for this is converted by combustion into sulphuric acid, which seriously injures pictures, furniture, &c. The object of the manufacturer of coal gas is to remove, as far as possible, everything from it, except the constituents mentioned as essential, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with good illuminating value.

The mode of purifying the gas, and the general arrangements for its manufacture, will be described in a later part of the work.

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* Including the benzene vapour, acetylene, &c. The coal gas of Paris has been found to contain as much as 3 per cent. by volume of vapour of benzene.

The destructive distillation of coal may be exhibited with the arrangement represented in fig. 122. The solid and liquid products (tar, ammoniacal liquor, &c.) are condensed in the globular receiver (A). The first bent tube contains, in one limb (B), a piece of red litmus-paper to detect ammonia; and in the other (C) a piece of paper impregnated with lead acetate, which will be blackened by the sulphuretted hydrogen. The second bent tube (D) contains enough lime-water to fill the bend, which will be rendered milky by the carbonic acid gas. The gas is collected over water, in the jar E, which is furnished with a jet from which the gas may be burnt when forced out by depressing the jar in water.

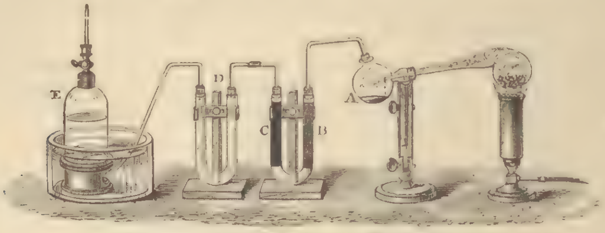

Fig. 122.—Destructive distillation of coal.

The presence of acetylene in coal gas may be shown by passing the gas from the supply-pipe (A, fig. 123), first through a bottle (B) containing a little ammonia, then through a bent tube (C) with enough water to fill the bend, and a piece of bright sheet copper immersed in the water in each limb. After a short time the bright red flakes of the copper acetylide will be seen in the water.

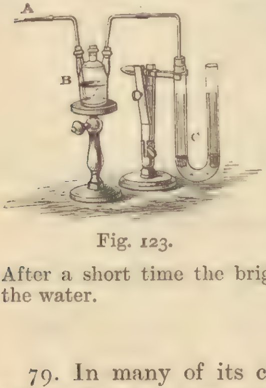

Fig. 123.

SILICON.

79. In many of its chemical relations to other bodies, this element will be found to bear a great resemblance to carbon; but whilst carbon is the characteristic element of organic substances, silicon is the most abundant in the mineral world, where it is chiefly found in combination with oxygen, as silica (SiO_2), either alone or as *silicates*.

Silica ($SiO_2 = 60$ parts by weight).—The purest natural form of silica is the transparent and colourless variety of quartz known as *rock crystal*, the most widely diffused ornament of the mineral world, often seen crystallised in beautiful six-sided prisms, terminated by six-sided pyramids (fig. 124), which are always easily distinguished by their great hardness, scratching glass almost as readily as the diamond. Coloured of a delicate purple, probably by a little organic matter, these crystals are known as *amethyst;* and when of a brown colour, as *Cairngorm stones* or *Scotch pebbles.* Losing its transparency and crystalline structure, we meet with silica in the form of *chalcedony* and of *carnelian*, usually coloured, in the latter, with oxide of iron.

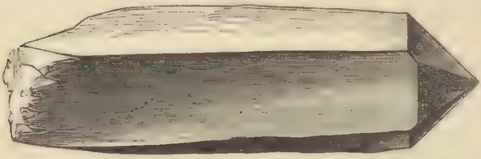

Fig. 124.—Crystal of quartz.

Hardly any substance has so great a share in the lapidary's art as silica, for in addition to the above instances of its value for ornamental purposes, we find it constituting *jasper*, *agate*, *cat's eye*, *onyx*, so much prized for cameos, *opal*, and some other precious stones. In opal the silica is combined with water.

Sand, of which the whiter varieties are nearly pure silica, appears to have been formed by the disintegration of siliceous rocks, and has generally a yellow or brown colour, due to the presence of oxide of iron.

The resistance offered by silica to all impressions has become proverbial in the case of *flint*, which consists essentially of that substance coloured with some impurity. Flints are generally found in compact masses, distributed in regular beds throughout the chalk formation; their hardness, which even exceeds that of quartz, formerly rendered them useful for striking sparks with steel, by detaching small particles of the metal, which are so heated by the percussion as to continue to burn (see p. 31) in the air, and to inflame tinder or gunpowder upon which they are allowed to fall.

The part taken by silica in natural operations appears to be chiefly a mechanical one, for which its stability under ordinary influences peculiarly fits it, for it is found to constitute the great bulk of the soil which serves as a support and food reservoir of land plants, and enters largely into the composition of the greater number of rocks.

But that this substance is not altogether excluded from any share in life, is shown by its presence in the shining outer sheath of the stems of the grasses and cereals, particularly in the hard external coating of the Dutch rush used for polishing; and this alone would lead to the inference that silica could not be absolutely insoluble, since the capillary vessels of plants are known to be capable of absorbing only such substances as are in a state of solution. Many natural waters also present us with silica in a dissolved state, and often in considerable quantity, as, for example, in the Geysers of Iceland, which deposit a coating of silica upon the earth around their borders.

Pure water, however, has no solvent action upon the natural varieties of silica. The action of an alkali is required to bring it into a soluble form.

To effect this upon the small scale, some white sand is very finely powdered (in an agate mortar), mixed with about four times its weight of dried sodium carbonate, placed upon a piece of platinum foil slightly

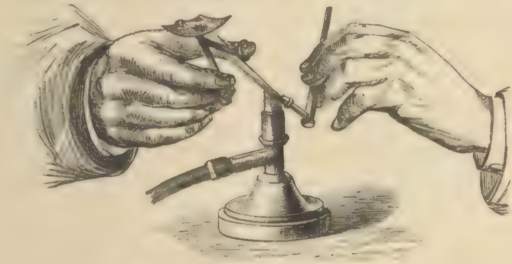

Fig. 125.—Fusion on platinum foil.

bent up (fig. 125), and fused by directing the flame of a blowpipe upon the under side of the foil. Effervescence will be observed, due to the escape of carbonic acid gas. The piece of platinum foil, when cool, may be placed in a little warm water, and allowed to soak for some time, when the melted mass will gradually dissolve, forming a solution of *sodium silicate.* This solution will be found decidedly alkaline to test-papers.

If a portion of the solution of sodium silicate in water be poured into a test-tube, and two or three drops of hydrochloric acid added to it, with occasional agitation, effervescence will be produced by the expulsion of any carbonic acid gas still remaining, and the solution will be converted into a gelatinous mass by the separation of silicic acid. But if another portion of the solution be poured into an excess of dilute hydrochloric acid (*i.e.*, into enough to render the solution distinctly acid), the silicic acid will remain dissolved in the water, together with the sodium chloride formed.

In order to separate the sodium chloride from the silicic acid, the process of *dialysis* * must be resorted to.

Dialysis is the separation of dissolved substances from each other by taking advantage of the different rates at which they pass through moist diaphragms or *septa.*

If the mixed solution of sodium chloride and silicic acid were poured upon an ordinary paper filter, it would pass through without alteration; but if parchment paper be employed, which is not pervious to water, although readily moistened by it, none of the liquid will pass through. If the cone of parchment paper be supported upon a vessel filled with distilled water (fig. 126), so that the water may be in contact with the outer surface of the cone, the hydrochloric acid and the sodium chloride will pass through the substance of the parchment paper, and the water charged with them may be seen descending in dense streams from the outside of the cone. After a few hours, especially if the water be changed occasionally, the whole of the hydrochloric acid and sodium chloride will have passed through, and a pure solution of silicic acid in water will remain in the cone.

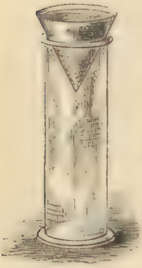

Fig. 126.

This solution is believed to contain the *orthosilicic acid*, H_4SiO_4. It is very feebly acid to blue litmus-paper, and not perceptibly sour to the taste. It has a great tendency to set into a jelly in consequence of the sudden separation of silicic acid. If it be slowly evaporated in a dish, it soon solidifies; but, by conducting the evaporation in a flask so as to prevent any drying of the silicic acid at the edges of the liquid, it may be concentrated until it contains 14 per cent. of silicic acid. When this solution is kept, even in a stoppered or corked bottle, it sets into a transparent gelatinous mass, which gradually shrinks and separates from the water. When evaporated, *in vacuo*, over sulphuric acid, it gives a transparent lustrous glass which is composed of 22 per cent. of water and 78 per cent. of silica ($H_2O.SiO_2$). This is also the composition of the gelatinous precipitate produced by acids in the solution of sodium silicate. It is sometimes written H_2SiO_3, and called *metasilicic acid.*

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* From διαλύω, to part asunder.

This hydrated silica cannot be redissolved in water, and is only soluble to a slight extent in hydrochloric acid. If it be heated to expel the water, the silica which remains is insoluble both in water and in hydrochloric acid, but is dissolved when boiled with solution of potash or soda, or their carbonates.

Silica in the naturally crystallised form, as rock crystal and quartz, is insoluble in boiling solutions of the alkalies, and in all acids except hydrofluoric; but amorphous silica (such as that found at Farnham) is readily dissolved by boiling alkalies. These represent, in fact, two distinct modifications of silica. A transparent piece of rock crystal may be heated to bright redness without change, but if it be powdered previously to being heated, its specific gravity is diminished from 2.6 to 2.4, and it becomes soluble in boiling alkalies, having been converted into the amorphous modification.

Crystals of quartz have been obtained artificially by the prolonged action of water upon glass at a high temperature under pressure. When fused with the oxyhydrogen blowpipe, silica does not crystallise, being thus converted into the amorphous variety of sp. gr. 2.3.

To prepare the amorphous modification of silica artificially, white sand in very fine powder may be fused, in a platinum crucible, with six times its weight of a mixture of equal weights of the potassium and sodium carbonates, the mixture being more easily fusible than either of the carbonates separately. The crucible may be heated over a gas burner supplied with a mixture of gas and air, or may be placed in a little calcined magnesia contained in a fireclay crucible, which may be covered up and introduced into a good fire. The platinum crucible is never heated in direct contact with fuel, since the metal would become brittle by combining with carbon, silicon, and sulphur derived from the fuel. The magnesia is used to protect the platinum from contact with the clay crucible. When the action of the silica upon the alkaline carbonates is completed, which will be indicated by the cessation of the effervescence, the platinum crucible is allowed to cool, placed in an evaporating dish, and soaked for a night in water, when the mass should be almost entirely dissolved. Hydrochloric acid is then added to the solution, with occasional stirring, until it is distinctly acid to litmus-paper. On evaporating the solution, it will, at a certain point, solidify to a gelatinous mass of hydrated silica, which would be spirted out of the dish if evaporation over the

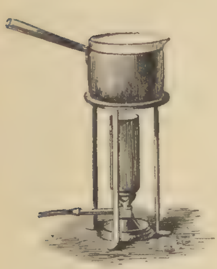

Fig. 127.

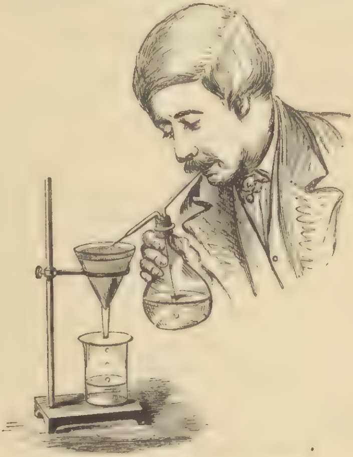

Fig. 128.—Washing a precipitate.

flame were continued. To prevent this, the dish is placed over an empty iron saucepan (fig. 127) so that the heat from the flame may be equally distributed over the bottom of the dish. When the mass is quite dry, the dish is allowed to cool, and some water is poured into it, which dissolves the chlorides of potassium and sodium (formed by the action of the hydrochloric acid upon the silicates), and leaves the silica in white flakes. These may be collected upon a filter (fig. 128), and washed several times with distilled water. The filter is then carefully spread out upon a hot iron plate, or upon a hot brick, and allowed to dry, when the silica is left as a dazzling white powder, which must be strongly heated in a porcelain or platinum crucible to expel the last traces of water. It is remarkable for its extreme lightness, especially when heated, the slightest current of air easily blowing it away.

80. For effecting such fusions as that just described, an air-gas blowpipe (A, fig. 129) supplied with air from a double action bellows (B), worked by a treadle (C), will be found most convenient. Where gas is not at hand, the fusion may be effected in a small furnace (fig. 130), surmounted with a conical chimney, and fed with charcoal.

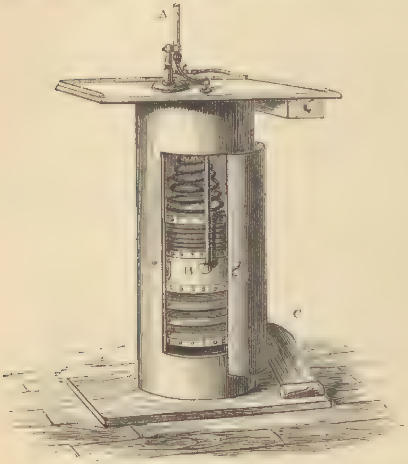

Fig. 129.—Air-gas blowpipe table.

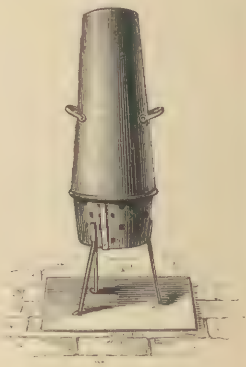

Fig. 130.—Charcoal furnace.

81. *Silicates.*—The acid properties of silicic acid are so feeble that it is a matter of great difficulty to determine the proportion of any base which is required to react with it in order to form a chemically neutral salt. Like carbonic acid, it does not destroy the action of the alkalies upon test-papers, and we are therefore deprived of this method of ascertaining the proportion of alkali which neutralises it in a chemical sense. In attempting to ascertain the quantity of alkali with which silica combines, from that of the carbon dioxide which it expels when heated with an alkaline carbonate, it is found that the proportion of carbon dioxide expelled varies considerably, according to the temperature and the proportion of alkaline carbonate employed.

By heating silica with sodium hydrate ($NaHO$), it is found that 60 parts of silica expel 36 parts of water, however much sodium hydrate is employed, and the same proportion of water is expelled from barium hydrate, $Ba(HO)_2$, when heated with silica.

The formula SiO_2 represents 60 parts by weight of silica, and 36 parts represent two molecules of water. Hence it would appear that the action of silica upon sodium hydrate is represented by the equation, $4NaHO + SiO_2 = Na_4SiO_4 + 2H_2O$; and that upon barium hydrate by $2Ba(HO)_2 + SiO_2 = Ba_2SiO_4 + 2H_2O$: and since it is found that several of the crystallised mineral silicates contain a quantity of metal equivalent to H_4, it is usual to represent silicic acid as a *tetrabasic* acid, H_4SiO_4, containing 4 atoms of hydrogen which may be replaced by metals.

The circumstance that silica is not capable of being converted into vapour at a high temperature, enables it to decompose the salts of many acids which, at ordinary temperatures, are able to displace silicic acid.

The silicates form by far the greatest number of minerals. The different varieties of clay consist of aluminium silicate; felspar is a silicate of aluminium and potassium; meerschaum is a silicate of magnesium.

The different kinds of glass are composed of silicates of potassium, sodium, calcium, lead, &c. None but the silicates of the alkali metals are soluble in water.

Scarcely any of the silicates are represented by formulæ which express their derivation from the acid H_4SiO_4; they are generally represented as combinations of metallic oxides with SiO_2.

82. *Silicon* or *silicium* ($Si = 28$ parts by weight).—From the remarkably unchangeable character of silica, it is not surprising that it was long regarded as an elementary substance. In 1813, however, Davy succeeded in decomposing it by the action of potassium, and in obtaining an impure specimen of silicon. It has since been produced, far more easily, by converting the silica into potassium silico-fluoride (K_2SiF_6), and decomposing this at a high temperature with potassium or sodium, which combines with the fluorine to form a salt capable of being dissolved out by water, leaving the silicon in the form of a brown powder (*amorphous silicon*), which resists the action of all acids, except hydrofluoric, which it decomposes, forming silicon fluoride, and evolving hydrogen ($Si + 4HF = SiF_4 + H_4$). It is also dissolved by solution of potash, with evolution of hydrogen, and formation of potassium silicate. It burns brilliantly when heated in oxygen, but not completely, for it becomes coated with silica which is fused by the intense heat of the combustion. When heated with the blowpipe on platinum foil, it eats a hole through the metal, with which it forms the fusible platinum silicide.

If potassium silico-fluoride be fused with aluminium, a portion of the latter combines with the fluorine, and the remainder combines with the silicon, forming aluminium silicide. By boiling this with hydrochloric and hydrofluoric acids in succession, the aluminium is extracted, and crystalline scales of silicon, with a metallic lustre resembling black lead, are left (*graphitoid silicon*). In this form the silicon has a specific gravity of about 2.5, and refuses to burn in oxygen, or to dissolve in hydrofluoric acid. A mixture of nitric and hydrofluoric acids, however, is capable of dissolving it. Like graphite, this variety of silicon conducts electricity, though amorphous silicon is a non-conductor. The amorphous silicon becomes converted into this incombustible and insoluble form under the action of intense heat. It is worthy of remark that the combustibility of amorphous carbon (charcoal) is also very much diminished by exposure to a high temperature.

Unlike carbon, however, silicon is capable of being fused at a temperature somewhat above the melting-point of cast-iron; on cooling, it forms a brilliant metallic-looking mass, which may be obtained, by certain processes, crystallized in octahedra so hard as to scratch glass like a diamond.

In their chemical relations to other substances there is much resemblance between silicon and carbon. Silicon, however, is capable of displacing carbon, for if potassium carbonate be fused with silicon, the latter is dissolved, forming potassium silicate, and carbon is separated. Silicon also resembles carbon in its disposition to unite with certain metals to form compounds which still retain their metallic appearance. Thus silicon is found together with carbon in cast-iron, and it unites directly with aluminium, zinc, and platinum, to form compounds resembling metallic alloys. Nitrogen enters into direct union with silicon at a high temperature, though it refuses to unite with carbon except in the presence of alkalies.

Silicon nitride (SiN) has been obtained by heating silica with carbon in a blast furnace, and treating the product successively with hydrofluoric acid and potash, when the nitride is left as a green infusible powder which is attacked by potash at a red heat, yielding potassium silicate, hydrogen, and ammonia. When heated in chlorine, it is converted into a white substance soluble in hydrofluoric acid, and apparently containing Si_3N_4. A similar body is also formed in the preparation of the green nitride.

In their relation to hydrogen, carbon and silicon are widely different, for silicon is only known to form one compound with hydrogen, and that of a very unstable character.

The *silicon hydride*, prepared by decomposing magnesium silicide with dilute hydrochloric acid, has been found to have a composition corresponding with the formula SiH_4. It derives its interest chiefly from the property of taking fire spontaneously in contact with the air, in which it burns with a brilliant white flame, giving off clouds of silica, and depositing a brown film of silicon upon a cold surface.

When cast-iron containing silicon is boiled with hydrochloric acid until the whole of the iron is dissolved, a grey frothy residue is left. If this be collected on a filter, well washed and dried, it is found to consist of black scales of graphite, mixed with a very light white powder. On boiling it with potash, hydrogen is evolved and the white powder dissolves, forming a solution containing potassium silicate. This white powder appears to be identical with a substance obtained by other processes, and called *leucone*,* which is believed to have the composition $Si_3H_4O_5$. Its action upon solution of potash would be explained by the equation—

$$Si_3H_4O_5 + 12KHO = 3K_4SiO_4 + H_6 + 5H_2O.$$

Leucone is slowly converted into silicic acid, even by the action of water, hydrogen being disengaged.

Another compound, containing silicon, hydrogen, and oxygen, has been named *silicone*. It is a yellow substance, the general characters of which resemble those of the compound last described. When exposed, under water, to the action of sunlight, hydrogen is evolved, and the yellow body becomes converted into leucone.

BORON.

83. Closely allied to silicon is another element, boron, which has at present never been found in animal or vegetable bodies, but appears to be entirely confined to the mineral kingdom.

Boric Anhydride, or *Anhydrous Boracic Acid* ($B_2O_3 = 69.8$ parts by weight).—A saline substance called *borax* ($Na_2B_4O_7.10Aq$) has long been used in medicine, in working metals, and in making imitations of precious stones; this substance was originally imported from India and

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* Λευκὸς, white.

Thibet, where it was obtained in crystals from the waters of certain lakes, and came into this country under the native designation of *tincal*, consisting of impure borax, surrounded with a peculiar soapy substance. Borax has recently been found in abundance in the bed of a dried-up lake in the Sierra Nevada. This lake is 15 miles long and 6 wide; the bed is a saline deposit 6 or 8 feet deep, with borax 3 feet deep at the edges, common salt in the centre, and sodium sulphate underneath.

In 1702, in the course of one of those experiments to which, though empirical in their nature, scientific chemistry is now so deeply indebted, Homberg happened to distil a mixture of borax and green vitriol (ferrous sulphate), when he obtained a new substance in pearly plates, which was found useful in medicine, and received the name of *sedative salt*. A quarter of a century later, Lemery found that this substance might be separated from borax by employing sulphuric acid instead of ferrous sulphate, and that it possessed acid properties, whence it was called boracic acid.

Much more recently this acid has been obtained in a free state from natural sources, and is now largely imported into this country from the volcanic districts in the north of Italy, where it issues from the earth in the form of vapour, accompanied by violent jets of steam, which are known in the neighbourhood as *soffioni*. It would appear easy enough, by adopting arrangements for the condensation of this steam, to obtain the boric acid which accompanies it, but it is found necessary to cause the steam to deposit its boric acid by passing it through water, for which purpose basins of brickwork (*lagunes*, fig. 131) are built up around the soffioni, and are kept filled with water from the neighbouring springs or brooks; this water is allowed to flow successively into the different lagunes, which are built upon a declivity for that purpose, and it thus becomes impregnated with about 1 per cent. of boric acid. The necessity for expelling a large proportion of this water, in order to obtain the boric acid in crystals, formed for a long time a great obstacle to the success of this branch of industry in a country where fuel is very expensive. In 1817, however, Larderello conceived the project of evaporating this water by the steam-heat afforded by the soffioni themselves, and several hundred tons of boric acid are now annually produced in this manner. The evaporation is conducted in shallow leaden evaporating pans (A, fig. 131), under which the steam from the soffioni is

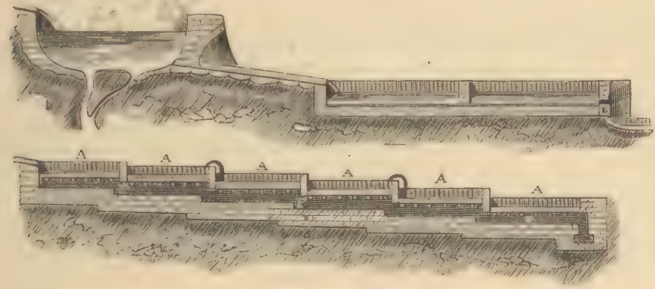

Fig. 131.—Boracic lagune and evaporating pans.

conducted through the flues (F) constructed for that purpose. As the demand for boric acid increased on account of the immense consumption of borax in the porcelain manufacture, the experiment was made, with success, of boring into the volcanic strata, and thus producing artificial soffioni, yielding boric acid.

The crystals of boric acid, as imported from these sources, contain salts of ammonia and other impurities. They dissolve in about three times their weight of boiling water, and crystallise out on cooling, since they require 26 parts of cold water to dissolve them. These crystals are represented by the formula $3H_2O.B_2O_3$ (or H_3BO_3). If they are sharply heated in a retort, they partly distil over unchanged, together with the water derived from the decomposition of another part; but if they be heated to 212° F. only, they effloresce, and become converted into $H_2O.B_2O_3$. When heated for a long time to 140° C., this becomes $H_2O.2B_2O_3$. This is sometimes written $H_2B_4O_7$, and called *pyroboric acid*, whilst $H_2O.B_2O_3$ is HBO_2, *metaboric acid*, and the crystals, H_3BO_3, are *orthoboric acid*. When pyroboric acid is heated further, the whole of the water passes off, carrying with it a little boric acid, and the B_2O_3 fuses to a glass, which remains perfectly transparent on cooling (*vitreous boric acid*). This is slowly volatilised by the continued action of a very high temperature. It dissolves very slowly in water. Boric acid is an *antiseptic*, *i.e.*, it hinders putrefaction, and is applied, either alone or in combination with glycerin, for the preservation of milk, meat, and other foods. It is also said to kill grass.

A characteristic property of boric acid is that of imparting a green colour to flames. Its presence may thus be detected in the steam issuing from a boiling solution of boric acid in water; for if a spirit-flame or a piece of burning paper be held in the steam, the flame will acquire a green tint, especially at the edges.

The colour is more distinctly seen when the cystallised boric acid is heated on platinum foil in a spirit-flame or an air-gas flame; and still better when the crystals are dissolved in boiling alcohol, and the solution burnt on a plate. The presence of boric acid in borax may be ascertained by mixing the solution of borax with strong sulphuric acid to liberate the boric acid, and adding enough alcohol to make the mixture burn; or by moistening the borax with glycerin, when it will give a green flame in the Bunsen burner. Another peculiar property of boric acid is its action upon turmeric. If a piece of turmeric paper be dipped in solution of boric acid and dried at a gentle heat, it assumes a fine brown-red colour, which is changed to green or blue by potash or its carbonate. In applying this test to borax, the solution is slightly acidified with hydrochloric acid, to set free the boric acid, before dipping the paper.

Borates.—Boric acid, like silicic, must be classed among the feeble acids. It colours litmus violet only, like carbonic acid, and does not neutralise the action of the alkalies upon test-papers. At high temperatures, fused boric anhydride combines with the alkalies and metallic oxides to form transparent glassy borates, which have, in many cases, very brilliant colours, and upon this property depend the chief uses of boric acid in the arts.

Unlike the silicates, the borates are comparatively rare in the mineral world. No very familiar mineral substance contains boric acid. A double borate of sodium and calcium, called *boro-natrocalcite*, $Na_2B_4O_7.(CaB_4O_7)_2.18H_2O$, is imported from Peru for the manufacture of borax, and the mineral known as *boracite* is a magnesium borate.

The mineral *tourmaline*, an aluminium-ferrous silicate, contains a considerable proportion of B_2O_3, apparently replacing part of the Al_2O_3.

In determining the proportion of base which boric acid requires to form a chemically neutral salt, the same difficulties are met with as in the case of silicic acid (p. 116); but since it is found that 69.8 parts of boric anhydride (the weight represented by B_2O_3) displace 54 parts of water (three molecules) from sodium hydrate and from barium hydrate, both employed in excess, it would appear that the boric acid requires three molecules of an alkali fully to satisfy its acid character.

The action of B_2O_3 upon an excess of NaHO would be represented by the equation $6NaHO + B_2O_3 = 2Na_3BO_3 + 3H_2O$. Hence, boric acid is a tribasic acid * represented by the formula H_3BO_3, which is the composition of the crystallised acid, but the formulæ of the common borates cannot be made to accord with this view. The only *orthoborate* yet obtained is $Mg_3(BO_3)_2$.

84. Boron ($B = 10.9$ parts by weight).—It was in the year 1808 that Gay-Lussac and Thénard succeeded, by fusing boric anhydride with potassium, in extracting from it the element boron, as an olive-green powder (*amorphous boron*), which has a general resemblance to silicon, but, unlike that element, may be oxidised by nitric acid. It also requires a higher temperature to fuse it than is required by silicon. The brilliant copper-coloured scales obtained by a process similar to that which furnished the graphitoid silicon, and formerly regarded as graphitoid boron, consist really of a compound of boron with aluminium.

The so-called *diamond of boron*, which is obtained by very strongly heating amorphous boron with aluminium, and afterwards extracting the aluminium from the mass with hydrochloric acid, contains aluminium and carbon combined with boron. These crystals are brilliant transparent octahedra, which are sometimes nearly colourless, and resemble the diamond in their power of refracting light, and in their hardness, which is so great that they will scratch rubies, and will even wear away the surface of the diamond.† This form of boron cannot be attacked by any acid, but is dissolved by fused alkalies. The flame of the oxyhydrogen blowpipe does not fuse it, and it only undergoes superficial conversion into boric anhydride when heated to whiteness in oxygen. When heated to redness in chlorine, however, it burns, forming boron trichloride. Boron closely resembles silicon in its chemical relations to the other elements. It forms a compound with hydrogen which is a spontaneously inflammable gas, burning with a green flame, and obtained by heating fused boric anhydride with magnesium and treating the mass with hydrochloric acid. Boron shows greater disposition to combine with nitrogen than is manifested by silicon. It absorbs nitrogen readily when heated to redness, forming a white infusible insoluble powder, the ***boron nitride*** (BN).

85. The elements carbon, boron, and silicon form a natural group, possessing many properties in common. They are all capable of existing in the amorphous and the crystalline forms; all incapable of being converted into vapour; all exhibit a want of disposition to dissolve; all form feeble acid oxides by direct union with oxygen; and all unite with

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* A *tribasic* acid is one which contains three atoms of hydrogen replaceable by metals.

† The author has known them to cut through the bottom of the beaker-glass used in separating them from the aluminium.

several of the metals to form compounds which resemble each other. Boron and silicon are capable of direct union with nitrogen, and so is carbon if an alkali be present. Recent researches attribute to silicon the power of occupying the place of carbon in some organic compounds, and the formulæ of leucone and silicone ($Si_3H_4O_5$ and $Si_6H_6O_4$) strongly remind us of the organic compounds of carbon with hydrogen and oxygen. In many of its physical and chemical characters silicon is closely allied with the metals, and it will be found that tin and titanium bear a particular resemblance to it in their chemical relations.

NITROGEN.

N = 14 parts by weight = 1 volume. 14 grains = 46.7 cub. in. at 60° F. and 30" Bar. 14 grammes = 11.16 litres at 0° C. and 760 mm. Bar.

86. This element, which has already been referred to as forming four-fifths of the volume of air, is elsewhere found in nature in the forms of saltpetre or potassium nitrate (KNO_3), and Chili saltpetre or sodium nitrate ($NaNO_3$). It also occurs as ammonia (NH_3) in the atmosphere and in the gaseous emanations from volcanoes. It is contained in the greater number of animal, and in many vegetable, substances, and therefore has a most important share in the chemical phenomena of life.

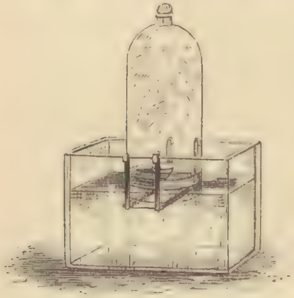
Fig. 132.—Preparation of nitrogen.

Nitrogen is generally obtained by burning phosphorus in a portion of air confined over water (fig. 132). The phosphorus is floated on the water in a small porcelain dish, kindled, and covered with a bell-jar. The nitrogen remains mixed with clouds of phosphoric anhydride (P_2O_5), which may be removed by allowing the gas to stand over water.

When nitrogen is required in larger quantity, it is more conveniently prepared by passing air from a gas-holder over metallic copper heated to redness in a tube. If the air be passed through solution of ammonia before passing over the heated copper, a short length of copper will suffice, since the oxide formed will be reduced by the ammonia; $3CuO + 2NH_3 = Cu_3 + 3H_2 + N_2$.

Nitrogen is also prepared by boiling a solution of ammonium nitrite (or mixed solutions of potassium nitrite and ammonium chloride); $NH_4NO_2 = 2H_2O + N_2$.

The remarkable chemical inactivity of free nitrogen has been alluded to in the chemistry of atmospheric air. It has been seen, however, to be capable of combining directly with boron and silicon, and magnesium and titanium unite with it even more readily at a high temperature. It is conspicuous among the elements for forming, with hydrogen, a powerful alkali (ammonia, NH_3), whilst the feeble chemical ties which hold it in combination with other elements, joined to its character of a permanent gas, render many of its compounds very unstable and explosive, as is the case with the so-called chloride and iodide of nitrogen, gun-cotton, the fulminates of silver and mercury, nitroglycerin, &c.

The discovery of nitrogen was made in 1772, by Rutherford (Professor of Botany in the University of Edinburgh), who was led to it by the observation that respired air was still unfit to support life when all the carbonic acid had been absorbed from it by a caustic alkali. Hence the name *azote* (ἀ, priv., and ζωή, life) formerly bestowed upon this gas.

Nitrogen has been liquefied by the cold produced by its expansion from a compression of 300 atmospheres at 13° C. Liquid nitrogen boils at − 193° C. under atmospheric pressure.

AMMONIA.

$NH_3 = 17$ parts by weight $= 2$ volumes.

87. Ammonia belongs to organic rather than to inorganic nature. It is generally a *post-mortem* product. Dead animal and vegetable matters yield it in *putrefaction*. Bones furnish it by *destructive distillation*; so does coal, the fossilised plant. Its compounds are found in beds of guano (the excrement of sea-fowl), and the most important of them, *sal-ammoniac*, was first made in Egypt from the dung of camels. Its mineral sources are chiefly volcanic; ammonium sulphate is found in Tuscan boric acid (p. 120), and occurs as *mascagnine* in the form of an efflorescence on recent lavas. It may be produced by the combination of nitrogen and hydrogen, induced by electric discharge, but its formation soon stops unless it is absorbed by an acid as fast as it is produced.

The proportion of ammonia existing in atmospheric air is so small that it is difficult to determine it with precision; it appears, however, not to exceed one-hundredth of a grain in a cubic foot,* for although ammonia is constantly sent forth into the air by the putrefaction of animal and vegetable substances containing nitrogen, it is soon absorbed by water, and even by earth and other porous solids. Rain-water contains from 1 to 2 parts per million of ammonia. Plants do not appear to be capable of absorbing from the atmosphere the nitrogen which it contains so abundantly in the uncombined form, but to derive their chief supply of that element from the ammonia and nitrates or nitrites contained in the air, the soil, and the water. During the life of an animal, it restores to the air the nitrogen which formed part of its wasted organs, in part directly as ammonia in the breath and in the exhalation from the skin,† whilst another portion is separated as urea and uric acid in the urine, to be eventually converted into ammonia when the excretion undergoes putrefaction. Dead animal and vegetable matter, when putrefying, restores its nitrogen to the air, chiefly in the forms of ammonia and substances closely allied to it, but partly also, it is said, in the free state. Ammonia appears to be formed from atmospheric nitrogen by the growth of fungi (which evolve hydrogen) and by the decay of wood. Nitrogen is also slowly absorbed from air by sawdust mixed with lime and by glucose mixed with soda; the nitrogen being evolved as ammonia when these materials are afterwards heated with soda-lime.

The *liquor ammoniæ*, or solution of ammonia in water, which is so largely used in medicine and the arts, is obtained chiefly from the

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* Recent determinations have given as much as 0.4 grain.

† Some doubt exists as to the exhalation of ammonia from the lungs and skin of man under normal conditions.

ammoniacal liquor resulting from the destructive distillation of coal for the manufacture of gas. The ammoniacal liquor of the gas-works contains ammonia in combination with carbonic and hydrosulphuric acid. As the first step towards extracting the ammonia in a pure state, the liquor is neutralised with hydrochloric acid, which combines with the ammonia, expelling the carbonic and hydrosulphuric acid gases. Since the latter has a very bad smell and is injurious to health, the neutralisation is generally effected in covered vats furnished with pipes, which convey the gases into a furnace where the hydrosulphuric acid is burnt, forming water and sulphurous acid gas. The solution is evaporated to expel part of the water, and allowed to cool in wooden vessels lined with lead, where ammonium chloride is deposited in crystals which contain a good deal of tarry matter. These crystals are moderately heated in an iron pan to deprive them of tar, and are finally purified by *sublimation*, that is, by converting them into vapour and allowing this vapour to condense again into the solid form. For this purpose the crystals are heated in a cylindrical iron vessel covered with an iron dome lined with fireclay. The ammonium chloride rises in vapour below a red heat, and condenses upon the dome in the form of the fibrous cake known in commerce as *sal ammoniac*.

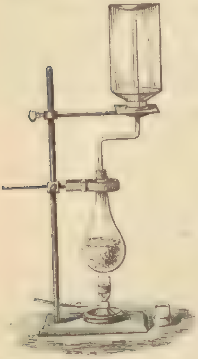
Fig. 133.—Preparation of ammonia.

To obtain ammonia from this salt, an ounce of it is reduced to coarse powder, and rapidly mixed with 2 ounces of powdered quicklime. The mixture is gently heated in a dry Florence flask (fig. 133), and the gas being little more than half as heavy as air (sp. gr. 0.59) may be collected in dry bottles by displacement of air, the bottles being allowed to rest upon a piece of tin plate which is perforated for the passage of the tube. To ascertain when the bottles are filled, a piece of red litmus-paper may be held at some little distance above the mouth, when it will at once acquire a blue colour if the ammonia escapes. The bottles should be closed with greased stoppers.

The action is explained by the following equation:

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Lime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + \underset{\text{Ammonia.}}{2NH_3}$$

The readiest method of obtaining gaseous ammonia for the study of its properties consists in gently heating the strongest *liquor ammoniæ* in a retort or flask provided with a bent tube for collecting the gas by displacement (fig. 134). The gas is evolved from the solution at a very low temperature, and may be collected unaccompanied by steam.

Ammonia is readily distinguished by its very characteristic smell, and its powerful alkaline action upon red litmus and turmeric papers. It is absorbed by water in greater proportion by volume than any other common gas, one volume of water absorbing more than 700 volumes of ammonia at the ordinary temperature, and becoming 1½ volume of solution of ammonia. No chemical combination appears to take place between the water and ammonia, for the gas gradually escapes on exposing the solution to the air, and no definite compound of the two has been noticed. Moreover, the quantity of ammonia retained by the water is dependent upon the temperature and pressure, as would be expected if the ammonia were merely *dissolved* and not combined with the water. The escape of the gas from the solution is attended with great production of cold, much heat becoming latent in the conversion of the ammonia from the liquid to the gaseous state.

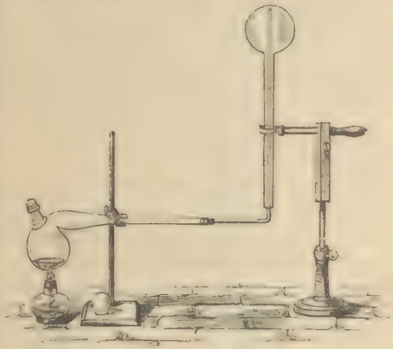
Fig. 134.

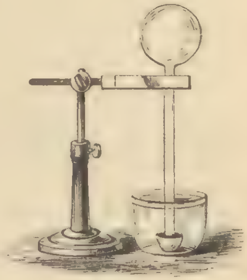
Fig. 135.

The rapid absorption of ammonia by water is well shown by filling a globular flask (fig. 135) with the gas, keeping it with its mouth downwards in a small capsule of mercury which is placed in a large basin. If this basin be filled with water, it cannot come into contact with the ammonia until the mouth of the flask is raised out of the mercury, when the water will quickly enter and fill the flask. The water should be coloured with reddened litmus to exhibit the alkaline reaction of the ammonia.

That the amount of ammonia in solution varies with the pressure, may be proved by filling a barometer tube, over 30 inches long, with mercury to within an inch of the top, filling it up with strong ammonia, closing the mouth of the tube, and inverting it with its mouth under mercury; on removing the finger, the diminished

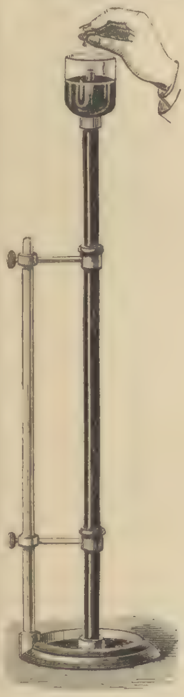
Fig. 136.

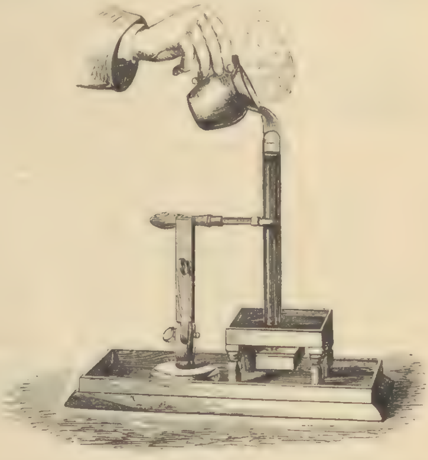
Fig. 137.

pressure caused by the gravitation of the column of mercury in the tube will cause the solution of ammonia to boil, from the escape of a large quantity of the gas, which will rapidly depress the mercury. If the pressure be now increased by gradually depressing the tube in a tall cylinder of mercury (fig. 136), the water will again absorb the ammoniacal gas.

To exhibit the easy expulsion of the ammoniacal gas from water by heat, a moderately thick glass tube, about 12 inches long and ½ inch in diameter, may be nearly filled with mercury, and then filled up with strong solution of ammonia; on closing it with the thumb, and inverting it into vessel of mercury (fig. 137), the solution will, of course, rise above the mercury to the closed end of the tube. By grasping this end of the tube in the hand, a considerable quantity of gas may be expelled, and the mercury will be depressed. If a little hot water be poured over the top of the tube, the latter will become filled with ammoniacal gas, which will be absorbed again by the water when the tube is allowed to cool, the mercury returning to fill the tube.

The solution of ammonia, which is an article of commerce, may be prepared by conducting the gas into water contained in a two-necked bottle, the second neck being connected with a tube passing into another bottle containing water, in which any escaping ammonia may be condensed. The strength of the solution is inferred from its specific gravity, which is lower in proportion as the quantity of ammonia in the solution is greater.

Thus, at 57° F., a solution of sp. gr. 0.8844 contains 36 parts by weight of ammonia in 100 parts of solution (*liquor ammoniæ fortissimus*); the sp. gr. 0.8976 indicates 30 per cent.; 0.9106, 25 per cent.; 0.9251, 20 per cent.; 0.9414, 15 per cent.; 0.9593, 10 per cent. (*British Pharmacopœia*); 0.979, 5 per cent. The specific gravity is ascertained by comparing the weights of equal volumes of water and of the solution at the same temperature. For this purpose a light stoppered bottle is provided, capable of containing about two fluid ounces. This is thoroughly dried, and counterpoised in a balance by placing in the opposite pan a piece of lead, which may be cut down to the proper weight. The bottle is then filled with solution of ammonia, the temperature observed with a thermometer and recorded, the stopper inserted, and the bottle weighed. It is then well rinsed out, filled with distilled water, the temperature equalised with that of the ammonia by placing the bottle either in warm or cold water, and the weight ascertained as before. The specific gravity is obtained by dividing the weight of the solution of ammonia by that of the water. The *ammonia meter* (fig. 138) is a convenient instrument for rapidly ascertaining the specific gravity of liquids lighter than water. It consists of a hollow glass float with a long stem, weighted with a bulb containing shot or mercury, so that when placed in distilled water it may sink to 1000° of the scale marked on the stem, this number representing the specific gravity of water. When placed in a liquid lighter than water, it must, of course, sink lower in order to displace more liquid (since solids sink until they have displaced their own weight of liquid). By trying it in liquids of known specific gravities, the mark upon the scale to which it sinks may be made to indicate the specific gravity of the liquid. The ammonia meter generally has a scale so divided that it indicates at once the percentage weight of ammonia. In this country the specific gravity of a liquid is always supposed to be taken at 62° F.

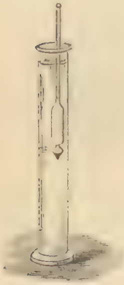

Fig. 138.

The common name for solution of ammonia, *spirit of hart's horn*, is derived from the circumstance that it was originally obtained for medicinal purposes by distilling shavings of that material.

When ammonia is exposed to a temperature of − 40° F. (*i.e.*, 72° below the freezing-point), or to a pressure of 6¼ atmospheres at 50°, it condenses to a clear liquid, which solidifies at a temperature of − 103° F. to a white crystalline mass. The comparative ease with which it may be liquefied has led to its application in Carré's freezing apparatus (fig. 139), in which the gas generated by heating a concentrated solution of ammonia in a strong iron boiler (A) is liquefied by its own pressure in an iron receiver (B) placed in cold water. When the boiler is taken off the fire and cooled in water, the liquefied ammonia evaporates very rapidly from the receiver back into the boiler, thereby producing so much cold that a vessel of water (C) placed in spirit of wine contained in a cavity in the receiver, is at once congealed into ice. A refrigerator constructed upon this principle is employed in the *salt gardens* of the south of France, in order to render their crystallising operations independent of the temperature of the air.

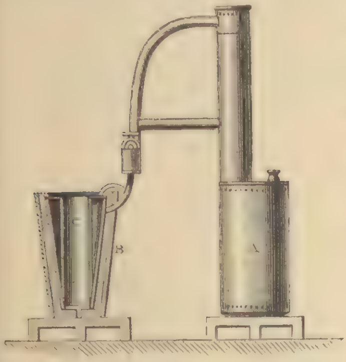

Fig. 139.—Carré's freezing apparatus.

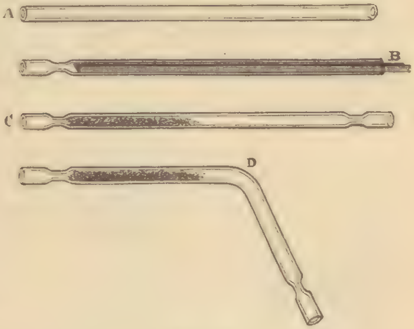

Fig. 140.

The liquefaction of ammonia is very easily effected by heating the ammoniated silver chloride in one limb of a sealed tube, the other limb of which is cooled in a freezing mixture. A piece of stout light green glass tube (A, fig. 140), about 12 inches long and ½ inch in diameter, is drawn out, at about an inch from one end, to a narrow neck. About 300 grains of silver chloride (dried at 400° F.) are introduced into the tube, so as to lie loosely in it. For this purpose a gutter of stiff paper (B) should be cut so as to slide loosely in the tube, the silver chloride placed upon it, and when it has been thrust into the tube (held horizontally) the latter should be turned upon its axis, so that the silver chloride may fall out of the paper, which may be then withdrawn. The tube is now drawn out to a narrow neck at about an inch from the other end, as in C, and afterwards carefully bent, as in D, care being taken that none of the chloride falls into the short limb of the tube, which should be about 4 inches long. The tube is then supported by a holder, so that the long limb may be horizontal, and is connected by a tube and

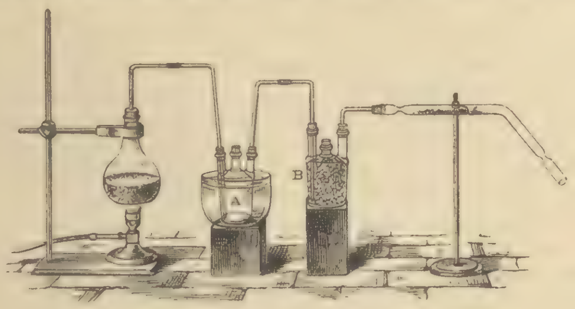

Fig. 141.

cork with an apparatus delivering dry ammonia, prepared by heating 1000 grains of sal ammoniac with an equal weight of quicklime in a flask, and passing the gas, first into an empty bottle (A, fig. 141) standing in cold water, and afterwards through a bottle (B) filled with lumps of quicklime to absorb all aqueous vapour. The long limb of the tube must be surrounded with filtering paper, which is kept wet with cold water. The current of ammonia should be continued at a moderate rate, until the tube and its contents no longer increase in weight, which will occupy about three hours—about 35 grains of ammonia being absorbed. The longer limb is sealed by the blowpipe flame whilst the gas is still passing, and then, as quickly as possible, the shorter limb, keeping that part of the tube which is occupied by the ammoniated silver chloride still surrounded by wet paper.

When the shorter limb of this tube is cooled (fig. 142), in a mixture of ice and salt (or of 8 ounces of sodium sulphate and 4 measured ounces of common hydrochloric acid), whilst the longer limb is gently heated from end to end by waving a spirit-flame beneath it, the ammonia evolved by the heat from the ammoniated silver-chloride, which partly fuses, will condense into a beautifully clear liquid in the cold limb. When this is withdrawn from the freezing mixture, and the tube allowed to cool, the liquid ammonia will boil and gradually disappear entirely, the gas being again absorbed by the silver chloride, so that the tube is ready to be used again.

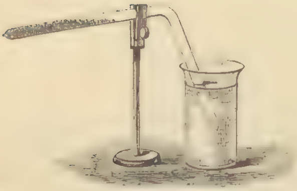

Fig. 142.—Liquefaction of ammonia.

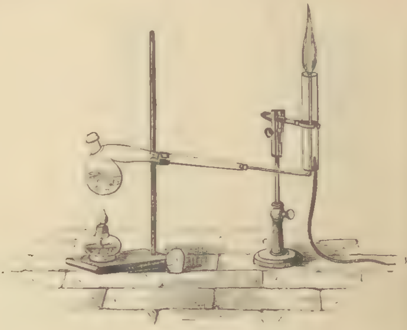

Fig. 143.

A small quantity of liquefied ammonia may be more conveniently obtained by means of a tube prepared as above, but containing about twelve inches of fragments of well-dried wood charcoal saturated with dried ammonia gas. The shorter limb of the tube should be drawn out to a long narrow point before sealing. This limb being immersed in the freezing mixture, the other is placed in a long test-tube containing water, which is heated to boiling. The ammonia soon returns to the charcoal when the tube cools.

Liquefied ammonia dissolves potassium and sodium to a blue solution; iodine, sulphur, and phosphorus are also dissolved by it.

Ammonia is feebly combustible in atmospheric air, as may be seen by holding a taper just within the mouth of an inverted bottle of the gas, which burns with a peculiar livid flickering light around the flame, but will not continue to burn when the flame is removed, because the temperature produced by the combustion of the hydrogen in air is not high enough to continue the decomposition. During its combustion the hydrogen is converted into water, and the nitrogen set free. In oxygen, however, ammonia burns with a continuous flame.

This is very well shown by surrounding a tube delivering a stream of ammonia (obtained by heating strong solution of ammonia in a retort) with a much wider tube open at both ends (fig. 143) through which oxygen is passed by holding a flexible tube from a gas-bag or gas-holder underneath it. On kindling the stream of ammonia it will give a steady flame of 10 or 12 inches long.

A similar experiment may be made with a smaller supply of oxygen, by lowering the tube delivering ammonia into a bottle or jar of oxygen, and applying a light to it just as it enters the mouth of the jar (fig. 144).

The elements of ammonia are easily separated from each other by passing the gas through a red-hot tube, or still more readily by exposing it to the action of the high temperature of the electric spark, when the volume of the gas rapidly increases until it is doubled, 2 volumes of ammonia being decomposed into 1 volume of nitrogen and 3 volumes of hydrogen.

For this experiment, a measured volume of ammonia gas is confined over mercury (fig. 145), in a tube through which platinum wires are sealed for the passage of the spark from an induction-coil. The volume of the gas is doubled in a few minutes, and if the tube be furnished with a stop-cock (A), the presence of free hydrogen may be shown by filling the open limb with mercury and kindling the gas as it issues from the jet.[*] A little NH_3 is always found undecomposed by the sparks; because, if a mixture of nitrogen with 3 vols. hydrogen be sparked, a little NH_3 is always produced, and if sulphuric acid be present to absorb the NH_3, the whole of the N and H_3 may be combined. A mixture of N and H_3 and a minute quantity of NH_3 is not affected by the spark.

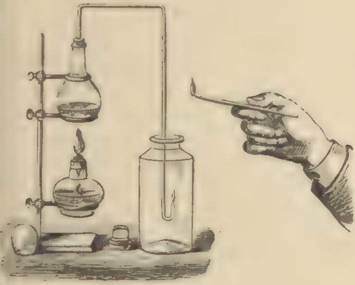

Fig. 144.

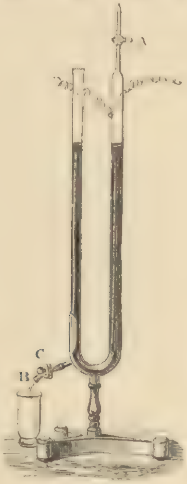

Fig. 145.

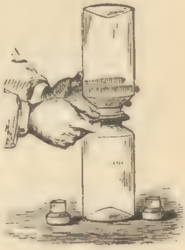

Fig. 146.

As might be expected from its powerfully alkaline character, ammonia exhibits a strong attraction for acids, which it neutralises perfectly. If a bottle of ammonia gas, closed with a glass plate, be inverted over a similar bottle of hydrochloric acid gas, and the glass plates withdrawn (fig. 146), the gases will combine, with disengagement of much heat, forming a white solid, ammonium chloride (NH_4Cl), in which the acid and alkali have neutralised each other. Again, if ammonia be added to diluted sulphuric acid, the latter will be entirely neutralised, and by evaporating the solution, crystals of ammonium sulphate, $(NH_4)_2SO_4$, may be obtained.

The substances thus produced by neutralising the acids with solution of ammonia bear a strong resemblance to the salts formed by neutralising the same acids with solutions of potash and soda, a circumstance which would encourage the idea that the solution of ammonia must contain an alkaline hydrate similar to KHO or $NaHO$.

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[*] The eudiometer for passing electric sparks in rapid succession must have the platinum wires passed through the glass as shown in fig. 145, or it will be cracked by the heat of the sparks. The outlet tube B, closed by a small screw clamp C, pinching a caoutchouc connector, allows the mercury to be drawn off when necessary, to equalise the level in the two limbs.

Berzelius was the first to make an experiment which appeared strongly to favour this view (commonly spoken of as the ammonium theory of Berzelius). The negative pole of a galvanic battery was placed in contact with mercury at the bottom of a vessel containing a strong solution of ammonia, in which the positive pole of the battery was immersed. Oxygen was disengaged at this pole, whilst the mercury in contact with the negative pole swelled to four or five times its original bulk, and became a soft solid mass, still preserving, however, its metallic appearance.* So far, the result of the experiment resembles that obtained when potassium hydrate is decomposed under similar circumstances, the oxygen separating at the positive pole, and the potassium at the negative, where it combines with the mercury. Beyond this, however, the analogy does not hold; for in the latter case the metallic potassium can be readily separated from the mercury, whilst in the former, all attempts to isolate the ammonium have failed, for the soft solid mass resolves itself, almost immediately after its preparation, into mercury, ammonia (NH_3), and hydrogen, one volume of the latter being separated for two volumes of ammonia. This would also tend to support the conclusion that a substance having the composition $NH_3 + H$ or NH_4 had united with the mercury; and since the latter is not known to unite with any non-metallic substance without losing its metallic appearance, it would be fair to conclude that the soft solid was really an amalgam of ammonium. However, the increase in the weight of the mercury is so slight, and the "amalgam," whether obtained by this or by other methods, is so unstable, that it would appear safer to attribute the swelling of the mercury to a physical change caused by the presence of the ammonia and hydrogen gases. This view is supported by the observation that when the amalgam is subjected to pressure its volume varies nearly in the inverse ratio of the pressure. It is difficult to believe that the solution of ammonia does really contain ammonium hydrate ($NH_3 + H_2O = NH_4HO$), when we find it evolving ammonia so easily; but it is equally difficult, upon any other hypothesis, to explain the close resemblance between the salts obtained by neutralising acids with this solution and those furnished by potash and soda.

The ordinary mode of exhibiting the production of the so-called *amalgam of ammonium* consists in acting upon the ammonium chloride (NH_4Cl) with sodium amalgam. A little pure mercury is heated in a test-tube, and a pellet of sodium thrown into it, when combination takes place with great energy. When the amalgam is nearly cool it may be poured into a larger tube containing a moderately strong solution of ammonium chloride; the amalgam at once swells to many times its former bulk, forming a soft solid substance lighter than the water, which may be shaken out of the tube as a cylindrical mass, decomposing rapidly with effervescence, evolving ammonia and hydrogen, and soon recovering its original volume and liquid condition.

88. *Atomic weight and volume of nitrogen.*—Two volumes (one molecule) of ammonia, when decomposed by a succession of electric

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* This experiment is more conveniently made with a strong solution of ammonium sulphate in a common plate. A sheet of platinum connected with the positive pole of the battery (five or six Grove's cells) is immersed in the solution, and a piece of filter-paper is laid upon it, on which is a globule of mercury into which the negative pole is plunged.

sparks, yield a mixture of one volume (one atom) of nitrogen, and three volumes (three atoms) of hydrogen. 22.4 litres of ammonia would yield 11.2 litres of nitrogen, weighing 14 grammes, and, since this is the smallest weight of nitrogen which can be found in 22.4 litres of any of its gaseous compounds, 14 is taken as the atomic weight of nitrogen.

89. *Formation of ammonia in the rusting of iron.*—Although free nitrogen and hydrogen can only with difficulty be made to form ammonia by direct combination, this compound is produced when the nitrogen meets with hydrogen in the *nascent* state; that is, at the instant of its liberation from a combined form. Thus, if a few iron filings be shaken with a little water in a bottle of air, so that they may cling round the sides of the bottle, and a piece of red litmus-paper be suspended between the stopper and the neck, it will be found to have assumed a blue colour in the course of a few hours, and ammonia may be distinctly detected in the rust which is produced. It appears that the water is decomposed by the iron in the presence of the carbonic acid of the air and water, and that the hydrogen liberated enters at once into combination with the nitrogen, held in solution by the water, to form ammonia.

If a few inches of magnesium tape be kindled and held over a plate to collect the product, it will be found to be a mixture of MgO and magnesium nitride, which evolves NH_3 when boiled with water; $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$.

In his experiments on the electrolysis of distilled water, Davy found that nitric acid was formed around the positive pole, by oxidation of the nitrogen of the air contained in the water, while ammonia was formed at the negative pole by combination of the hydrogen with nitrogen.

90. *Production of nitrous and nitric acids from ammonia.*—If a few drops of a strong solution of ammonia be poured into a pint bottle, and ozonised air (from the tube for ozonising by induction, fig. 48) be passed into the bottle, thick white clouds will speedily be formed, consisting of *ammonium nitrite*, the nitrous acid having been produced by the oxidation of the ammonia at the expense of the ozonised oxygen—

$$2NH_3 + O_3 = H_2O + \underset{\text{Ammonium nitrite.}}{NH_4NO_2}$$

If copper filings be shaken with solution of ammonia in a bottle of air, white fumes will also be produced, together with a deep blue solution containing copper oxide and ammonium nitrite; the act of oxidation of the copper appearing to have induced a simultaneous oxidation of the ammonia.

A coil of thin platinum wire made round a pencil, if heated to redness at the lower end and suspended in a flask (fig. 147) with a little strong ammonia at the bottom, will continue to glow for a great length of time, in consequence of the combination of the ammonia with the oxygen of the air taking place at its surface, attended with great evolution of heat. Thick white clouds of ammonium nitrite are formed, and frequently red vapour of nitrous anhydride (N_2O_3) itself. A coil of thin copper wire acts in a similar manner.

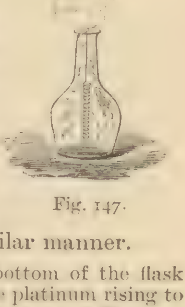

Fig. 147.

If a tube delivering oxygen gas be passed down to the bottom of the flask (fig. 148), the action will be far more energetic, the heat of the platinum rising to whiteness, when an explosion of the mixture of ammonia and oxygen will ensue.

After the explosion the action will recommence, so that the explosion will repeat itself as often as may be wished. It is unattended with danger if the mouth of the flask be pretty large.* By regulating the stream of oxygen, the bubbles of that gas may be made to burn as they pass through the ammonia at the bottom of the flask.

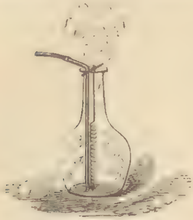

Fig. 148.

The oxidation of ammonia may also be shown by the arrangement represented in fig. 149. Air is slowly passed from the gas-bag B, through very weak ammonia in the bottle *a*, into a hard glass tube having a piece of red litmus-paper at *b*, and a plug of platinised asbestos in the centre, heated by a gas burner; a piece of blue litmus-paper is placed at *c*, and the tube is connected with a large globe (*d*). The red litmus at *b* is changed to blue by the ammonia, whilst the blue litmus at *c* is reddened by the nitrous acid produced in its oxidation, and clouds of ammonium nitrite, accompanied by red nitrous fumes, appear in *d*. To obtain all the results in perfection, small quantities of ammonia must be successively introduced into *a*.

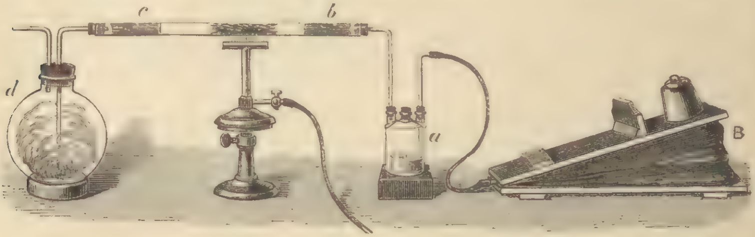

Fig. 149.—Oxidation of ammonia.

(The burner represented in the figure is a Bunsen burner (p. 107), surmounted by a T-piece with several holes.)

When hydrogen or coal gas burns in air, small quantities of nitrous and nitric acids are produced, apparently by the oxidation of atmospheric nitrogen.

In the presence of strong bases, and of porous materials to favour oxidation, ammonia is capable of suffering further oxidation and conversion into nitric acid, which acts upon the base to form a nitrate; thus, $2NH_3 + CaO + O_8 = \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + 3H_2O$.

91. This formation of nitrates from ammonia is commonly referred to as *nitrification*, and appears to be concerned in the formation of the natural supplies of saltpetre which are of so great importance to the arts.† Recent investigations indicate that the presence of some minute fungus or organised ferment plays an important part in the process.

This ferment consists of minute round or oval corpuscles, which appear to propagate by budding, like yeast. It is abundant in soils, in sewage, and in water contaminated with organic matter. Feeble alkalinity, such as is due to the presence of calcium carbonate, is favourable to its action.

When the nitrification of ammonia takes place in cold dilute solutions, in the dark, nitrates only are formed; but in the case of strong solutions, or at higher temperatures, or under exposure to light, nitrites are produced. The formation of nitrites or nitrates seems to depend, in part, upon the condition of the ferment; in some cases, it produces nitrites only, even if light be excluded. A solution of potassium nitrite may be converted into nitrate, in the dark, by adding a little solution in which nitrites have lately changed into nitrates, and which therefore contains the nitrifying ferment.*

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* It is advisable to surround the flask with a cylinder of coarse wire gauze.

† The charcoal which has been used in the sewer ventilators (see p. 69) has been found to contain abundance of nitrates.

COMPOUNDS OF NITROGEN AND OXYGEN.

92. Though these elements in their pure state exhibit no attraction for each other, six compounds, which contain them in different proportions, have been obtained by indirect processes, viz., N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5.

When a succession of strong electric sparks from the induction-coil is passed through atmospheric air in a dry flask (especially if the air be mixed with oxygen), a red gas, nitric peroxide (NO_2),† is formed; if water be present, this is absorbed and converted into nitrous and nitric acids; $2NO_2 + H_2O = HNO_2 + HNO_3$.

If the experiment be made in a graduated eudiometer (fig. 150), standing over water coloured with blue litmus, the latter will very soon be reddened by the acid formed, and the air will be found to diminish very considerably in volume, eventually losing its power of supporting combustion, in consequence of the removal of oxygen.

A U-tube having one limb surmounted by a stoppered globe into which platinum wires are sealed, allows the air to be tested with a small taper to show that the oxygen has been removed.

When a few inches of magnesium tape are burnt in a gas-jar of air, red fumes may be perceived on looking down the jar at the close of the combustion, and the presence of N_2O_3 or NO_2 may be shown by drawing the residual air through a mixture of potassium iodide with a little starch and acetic acid, when the iodine is set free and blues the starch. This renders it probable that the electric spark causes the combination of nitrogen and oxygen on account of its high temperature.

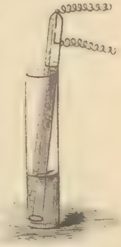
Fig. 150.

When ozonised air (p. 57) is passed into water, nitric acid is found in solution. Rain water contains about 1 part per million of nitric acid.

When hydrogen gas, mixed with a small quantity of nitrogen, is burnt, the water collected from it is found to have an acid taste and reaction, due to the presence of a little nitric acid, resulting from the combination of the nitrogen with the oxygen of the air under the influence of the intense heat of the hydrogen flame.

Since all the compounds of nitrogen and oxygen are obtained, in practice, from nitric acid, the chemical history of that substance must precede that of the oxides of nitrogen.

NITRIC ACID, OR HYDRIC NITRATE.

$HNO_3 = 63$ parts by weight $= 2$ vols.

93. This most important acid is obtained from saltpetre, which is found as an incrustation upon the surface of the soil in hot and dry climates, as in some parts of India and Peru. The salt imported into this country from Bengal and Oude consists of nitrate of potash or potassium nitrate (KNO_3), whilst the Peruvian or Chilian saltpetre is nitrate of soda or sodium nitrate ($NaNO_3$). Either of these will serve for the preparation of nitric acid.

On the small scale, in the laboratory, nitric acid is prepared by distilling potassium nitrate with an equal weight of concentrated sulphuric acid.

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* Warington on Nitrification, *Jour. Chem. Soc.*, 1879.

† Brodie has shown that perfectly dry air yields oxides of nitrogen under the influence of the induction tube (p. 57).

In order to make the experiment, four ounces of powdered nitre, thoroughly dried, may be introduced into a stoppered retort (fig. 151) and two and a half measured ounces of concentrated sulphuric acid poured upon it. As soon as the acid has soaked into the nitre, a gradually increasing heat may be applied by means of an Argand burner, when the acid will distil over. It must be preserved in a stoppered bottle.

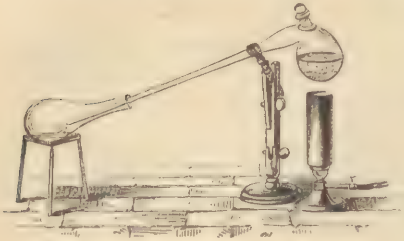

Fig. 151.—Preparation of nitric acid.

When the acid has ceased distilling, the retort should be allowed to cool, and filled with water. On applying a moderate heat for some time the saline residue will be dissolved. The solution may then be poured into an evaporating dish, and evaporated down to a small bulk. On allowing the concentrated solution to cool, crystals of bisulphate of potash or hydro-potassium sulphate ($KHSO_4$) are deposited, a salt which is very useful in many metallurgic and analytical operations.

The decomposition of potassium nitrate by an equal weight of sulphuric acid is explained by the equation—

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$

It would appear at first sight that one-half of the sulphuric acid might be dispensed with, but it is found that when less sulphuric acid is employed, so high a temperature is required to effect the complete decomposition of the saltpetre (the above equation then representing only the first stage of the action), that much of the nitric acid is decomposed; and the normal potassium sulphate (K_2SO_4), which would be the final result, is not nearly so easily dissolved out of the retort by water as the bisulphate.

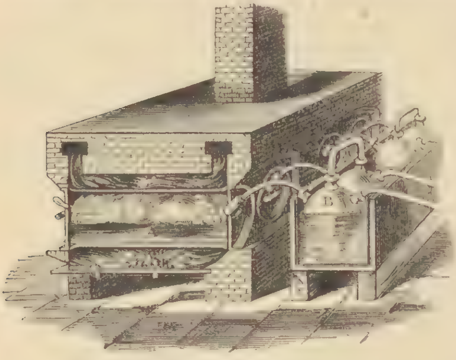

Fig. 152.—Preparation of nitric acid.

For the preparation of large quantities of nitric acid, sodium nitrate is substituted for potassium nitrate, being much cheaper, and furnishing a larger proportion of nitric acid.

The sodium nitrate is introduced into an iron cylinder (A, fig. 152) lined with fireclay to protect it from the action of the acid, and an equal weight of sulphuric acid (oil of vitriol) is poured upon it through a stoppered opening at the back. Heat is then applied by a furnace, into which the cylinders are built in pairs, when the nitric acid passes off in vapour, and is condensed in a series of stoneware bottles (B), surrounded with cold water.

In the preparation of nitric acid, it will be observed at the beginning and towards the end of the operation that the retort becomes filled with a red vapour. This is due to the decomposition by heat of a portion of the colourless vapour of nitric acid, into water, oxygen, and nitric peroxide, $2HNO_3 = H_2O + O + 2NO_2$, this last forming the red vapour, a portion of which is absorbed by the nitric acid, and gives it a yellow colour.

The pure nitric acid is colourless, but if exposed to sunlight it becomes yellow, a portion suffering this decomposition. In consequence of the accumulation of the oxygen in the upper part of the bottle, the stopper is often forced out suddenly when the bottle is opened, and care must be taken that drops of this very corrosive acid be not spirted into the face.

The strongest nitric acid (obtained by distilling perfectly dry nitre with an equal weight of pure oil of vitriol, and collecting the middle portion of the acid separately from the first and last portions, which are somewhat weaker) emits very thick grey fumes when exposed to damp air, because its vapour, though itself transparent, absorbs water very readily from the air, and condenses into very minute drops of diluted nitric acid which compose the fumes. The weaker acids commonly sold in the shops do not fume so strongly. An exact criterion of the strength of any sample of the acid is afforded by the specific gravity, which may be ascertained by the methods described for ammonia, using a hydrometer adapted for liquids heavier than water. Thus, the strongest acid (HNO_3) has the specific gravity 1.52;* whilst the ordinary *aquafortis* or diluted nitric acid has the sp. gr. 1.29, and contains only 46.6 per cent. of HNO_3. The concentrated nitric acid usually sold by the operative chemist (*double aquafortis*) has the sp. gr. 1.42, and contains 67.6 per cent. of HNO_3.

A very characteristic property of nitric acid is that of staining the skin yellow. It produces the same effect upon most animal and vegetable matters, especially if they contain nitrogen. The application of this in dyeing silk of a fast yellow colour may be seen by dipping a skein of white silk in warm diluted nitric acid, and afterwards immersing it in dilute ammonia, which will convert the yellow colour into a brilliant orange. When sulphuric or hydrochloric acid is spilt upon the clothes, a red stain is produced, and a little ammonia restores the original colour; but nitric acid stains are yellow, and ammonia intensifies instead of removing them, though it prevents the cloth from being eaten into holes.

Nitric acid changes most organic colouring matters to yellow, but, unless very concentrated, it merely reddens litmus. If solutions of indigo and litmus are warmed in separate flasks, and a little nitric acid added to each, the indigo will become yellow and the litmus red. Here the indigo (C_8H_5NO) acquires oxygen from the nitric acid, and is converted into *isatine* ($C_8H_5NO_2$).

When nitric acid is heated, it begins to boil at 184° F. (84° C.), but it cannot be distilled unchanged, for a considerable quantity is decomposed into nitric peroxide, oxygen, and water, the two first passing off in the gaseous form, whilst the water remains in the retort with the nitric acid, which thus becomes gradually more and more diluted, until it contains 68 per cent. of HNO_3, when it passes over unchanged at the temperature of 248° F. (120° C.). The specific gravity of this acid is 1.42. If an acid weaker than this be submitted to distillation, water will pass off until acid of this strength is obtained, when it distils over unchanged.

The specific gravity of the vapour of nitric acid, at 86° C., has been determined as 29.6 ($H = 1$), which is sufficiently near to half of 63, to show that the molecule HNO_3 would occupy exactly two volumes if it had not suffered partial decomposition by heat.

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* It is extremely difficult to obtain the HNO_3 free from any extraneous water, as it undergoes decomposition not only when vaporised at the boiling-point, but even as ordinary temperatures.

The facility with which nitric acid parts with a portion of its oxygen, renders it very valuable as an *oxidising agent.* Comparatively few substances which are capable of forming compounds with oxygen can escape oxidation when treated with nitric acid.

A small piece of phosphorus dropped into a porcelain dish containing the strongest nitric acid (and placed at some distance to avoid danger), soon begins to act upon the acid, generally with such violence as to burst out into flame, and sometimes to shatter the dish; the result of this action is phosphoric acid, the highest state of oxidation of phosphorus.

When sulphur is heated with nitric acid, it is actually oxidised to a greater extent than when burnt in pure oxygen, for in this case it is converted into sulphurous acid gas (SO_2), whilst nitric acid converts it into sulphuric acid, H_2SO_4.

Charcoal, which is so unalterable by most chemical agents at the ordinary temperature, is oxidised by nitric acid. If the strongest nitric acid be poured upon finely powdered charcoal, the latter takes fire at once.

Even iodine, which is not oxidised by free oxygen, is converted into iodic acid (HIO_3) by nitric acid.

But it is especially in the case of metals that the oxidising powers of nitric acid are called into useful application.

If a little black oxide of copper be heated in a test-tube with nitric acid, it dissolves, without evolution of gas, yielding a blue solution, which contains copper nitrate, $2HNO_3 + CuO = H_2O + Cu(NO_3)_2$.

But when nitric acid is poured upon metallic copper (copper turnings) very violent action ensues, red fumes are abundantly evolved, and the metal dissolves in the form of copper nitrate, nitric oxide being formed, $8HNO_3 + Cu_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$.

The nitric oxide itself is colourless, but as soon as it comes into contact with the oxygen of the air, it is converted into the red nitric peroxide, $NO + O = NO_2$.

The gases evolved when nitric acid is de-oxidised by the metals are nitric oxide, NO, nitrous oxide, N_2O, and nitrogen, in proportions which vary with the nature of the metal, the strength of the acid, and, to some extent, with the temperature.

Copper and silver, dissolved in nitric acid diluted with two parts of water, evolve nearly pure NO.

Iron also evolves nearly pure NO, when dissolved either in nitric acid with one part or with twelve parts of water.

Zinc, with 1 : 2 strength of acid, whether hot or cold, evolves nearly equal volumes of NO and N_2O, but with the strong acid it evolves scarcely any NO, but a mixture of about 2 vols. of N_2O and 1 vol. N.

Tin, with cold concentrated nitric acid, also evolves scarcely any NO, but a mixture of about 6 vols. N_2O and 1 vol. N.

All the metals in common use are acted upon by nitric acid, except gold and platinum, so that this acid is employed to distinguish and separate these metals from others of less value. The ordinary ready method of ascertaining whether a trinket is made of gold, consists in touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colours base alloys blue, from the formation of copper nitrate. The *touch-stone* allows this mode of testing to be applied with great accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold be drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; whilst the streak left by brass, or any similar base alloy, is rapidly dissolved by the acid. Experience enables an operator to determine, by means of the touch-stone, pretty nearly the amount of gold present in the alloy, comparison being made with the streaks left by alloys of known composition.

Though all the metals in common use, except gold and platinum, are *oxidised* by nitric acid, they are not all *dissolved;* there are two metals, tin and antimony, which are left by the acid in the state of insoluble oxides, which possess acid properties, and do not unite with the nitric acid.

If some concentrated nitric acid be poured upon tin, no action will be observed;* but on adding a little water, red fumes will be evolved in abundance, and the tin will be converted into a white powder, *metastannic acid.*

If the white mixture be stirred with slaked lime, the smell of ammonia will be exhaled; other metals also produce ammonia when dissolved in diluted nitric acid, its quantity increasing with the degree of dilution of the nitric acid; of course, the ammonia combines with the excess of acid present to form ammonium nitrate, and the lime was added in the above experiment in order to displace the ammonia from its combination, and to exhibit its odour. This conversion of nitric acid into ammonia becomes the more interesting when it is remembered that the ammonia can be reconverted into nitric acid (p. 132).

By dissolving zinc in very diluted nitric acid, a very large quantity of ammonia may be obtained. The change is easily followed if we suppose the *nascent* hydrogen, produced by the action of the zinc upon the water, to act upon the nitric acid, converting its oxygen into water, and its nitrogen into ammonia, thus—$HNO_3 + H_8 = 3H_2O + NH_3$. The exalted attractions possessed by substances in the nascent state, that is, at the instant of their passing from a state of combination, are very remarkable, and will be found to receive frequent application.

When a solution of potassium nitrate is mixed with a strong solution of caustic potash, and heated with granulated zinc, ammonia is abundantly disengaged, being produced by the nascent hydrogen resulting from the action of the zinc upon the caustic potash. Aluminium acts thus even in dilute solutions.

Action of nitric acid upon organic substances.—The oxidising action of nitric acid upon some organic substances is so powerful as to be attended with inflammation; if a little of the strongest nitric acid be placed in a porcelain capsule, and a few drops of oil of turpentine be poured into it from a test-tube fixed to the end of a long stick, the turpentine takes fire with a sort of explosion. By boiling some of the strongest acid in a test-tube (fig. 153), the mouth of which is loosely stopped with a plug of raw silk or of horsehair, the latter may be made to take fire and burn brilliantly in the vapour of nitric acid.

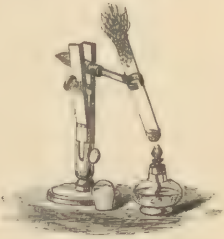

Fig. 153.

In many cases the products of the action of nitric acid exhibit a most interesting relation to the substances from which they have been produced, one or more atoms of the hydrogen of the original compound having been removed in the form of water by the oxygen of the nitric acid, whilst the spaces thus left vacant have been filled up by the nitric peroxide resulting from the de-oxidation of the nitric acid, producing what is termed a *nitro-substitution* compound. A very simple example of this displacement of H by NO_2 is afforded by the action of nitric acid upon benzene. A little concentrated nitric acid is placed in a flask, and benzene cautiously dropped into it; a violent action ensues, and the acid becomes of a deep red colour; if the contents of the flask be now poured into a large vessel of water, a heavy yellow oily liquid is separated, having a powerful odour, like that of bitter almond oil. This substance, which is used to a considerable extent in perfumery under the name of essence of Mirbane, is called *nitro-benzene*, and its formula, $C_6H_5(NO_2)$, at once exhibits its relation to benzene, C_6H_6.*

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* It is a fact which has scarcely been explained in a satisfactory manner, that the concentrated nitric acid often refuses to act upon metals which are violently attacked by the diluted acid.

But the change does not stop here, for by continuing the action of the acid, *dinitro-benzene*, $C_6H_4(NO_2)_2$, is obtained, in which two atoms of hydrogen have been displaced by nitric peroxide.

It is by an action of this description that nitric acid gives rise to gun-cotton, and other explosive substances of the same class, when acting upon the different varieties of woody fibre, as cotton, paper, saw-dust, &c.

The preparation and composition of gun-cotton will be described hereafter.

94. The oxidising effects of nitric acid are shared to some extent by the nitrates. A mixture of nitrate of lead with charcoal explodes when sharply struck, from the sudden evolution of carbonic acid gas, produced by the oxidation of the carbon. If a few crystals of copper nitrate be sprinkled with water and quickly wrapped up in tin-foil, the latter will, after a time, be so violently oxidised as to emit brilliant sparks.

But in the case of the nitrates of alkali metals, the oxidation takes place only at a high temperature. If a little nitre be fused in an earthen crucible or an iron ladle, and, when it is at a red heat, some powdered charcoal, and afterwards some flowers of sulphur, be thrown into it, the energy of the combustion will testify to the violence of the oxidation. In this manner the carbon is converted into potassium carbonate (K_2CO_3), and the sulphur into potassium sulphate (K_2SO_4). See *Gunpowder*.

95. *Anhydrous nitric acid* or *nitric anhydride* (N_2O_5) is obtained by gently heating silver nitrate in a slow current of chlorine, great care being taken to exclude every trace of water; $2AgNO_3 + Cl_2 = 2AgCl + O + N_2O_5$.

It may also be obtained by adding anhydrous phosphoric acid to the strongest nitric acid cooled in snow and salt, and carefully distilling at as low a temperature as possible into a receiver cooled in snow and salt.

The anhydride is condensed as a crystalline solid. It forms transparent colourless prisms which liquefy at 85° F., and boil at 113°. By a slightly higher temperature it is readily decomposed; and it has been said to decompose even at the ordinary temperature, in sealed tubes, which were shattered by the evolved gas. It is more stable in the dark.

When the anhydride is brought in contact with water, much heat is evolved, and nitric acid is produced.

The specific gravity of the vapour of nitric anhydride being unknown, it is only a surmise that its molecule is represented by N_2O_5. Its formation by the action of chlorine upon silver nitrate appears to take place in two stages—

(1) $Ag.O.NO_2 + Cl_2 = AgCl + NO_2Cl$ (*nitroxyle chloride*) $+ O$; and
(2) $NO_2Cl + Ag.O.NO_2 = AgCl + NO_2.O.NO_2$ (*nitric anhydride*).

The disposition of HNO_3 to give NO_2 as a product of its decomposition, and to exchange it for the hydrogen of organic substances, leads to the belief that it is

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$$^*\ C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O$$
$$C_6H_6 + 2(HNO_3) = C_6H_4(NO_2)_2 + 2H_2O.$$

really formed upon the type of a molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, in which half the hydrogen is displaced by NO_2. The relation between the anhydride, the acid, and the nitrates, would then be a very simple one; nitric anhydride $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$; nitric acid, $\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O$; saltpetre, $\left.\begin{matrix}K\\NO_2\end{matrix}\right\}O$.

Nitrates.—Its powerful action on bases places nitric acid among the strongest of the acids, though the disposition of its elements to assume the gaseous state at high temperatures, conjoined with the feeble attraction existing between nitrogen and oxygen, causes its salts to be decomposed, without exception, by heat. The nature of the decomposition varies with the metal contained in the nitrate. The nitrates of alkali metals are first converted into nitrites by the action of heat; thus KNO_3 gives KNO_2 and O; the nitrites themselves being eventually decomposed, evolving nitrogen and oxygen, and leaving the oxide of the metal. The nitrates of copper and lead evolve nitric peroxide (NO_2) and oxygen, the oxides being left. The nitrate of mercury leaves red oxide of mercury, which is decomposed at a higher temperature into mercury and oxygen.

Nitric acid is a *monobasic* acid, because it contains only one atom of hydrogen to be replaced by a metal. Comparatively few of the nitrates are in common use; the following table contains those most frequently used:—

Chemical Name.	Common Name.	Formula.
Potassium nitrate	Nitre, saltpetre	KNO_3
Sodium nitrate	Cubic nitre Peruvian saltpetre	$NaNO_3$
Strontium nitrate	Nitrate of strontian	$Sr(NO_3)_2$
Basic bismuth nitrate	Trisnitrate of bismuth Flake white	$Bi(NO_3)_3.2Bi(OH)_3$
Silver nitrate	Lunar caustic	$AgNO_3$

Determination of the composition of nitric acid.—A definite weight, say 10 grms., of pure lead oxide is taken, 5 grms. of nitric acid mixed with it, and a gentle heat applied as long as vapour of water escapes; $PbO + 2HNO_3 = H_2O + Pb(NO_3)_2$. Say that the residue weighs 14.27 grms.; then

From the weight of lead oxide and nitric acid	15.00 grms.
Deduct weight of lead oxide and lead nitrate	14.27 ,,
Water which has been expelled	.73 ,,

corresponding to .08 grm. H.

The mixture of lead nitrate and excess of lead oxide is then strongly heated in a tube containing copper, when $Pb(NO_3)_2 + Cu_5 = PbO + 5CuO + N_2$; the nitrogen is collected and measured. Say that 884.7 cub. cent. of N are obtained; these would weigh $884.7 \times \frac{14}{11160}$ grm. = 1.19 grm.

Hence we find, in 5 grms. of nitric acid, 1.19 grm. N, .08 grm. H, and, by difference, 3.73 grms. O. Dividing these numbers by the atomic weights, 14, 1, and 16, we obtain .08 atom of N, .08 atom of H, and .24 atom of O, or 1 atom of H, to 1 atom of N and 3 atoms of O. This would give, for the molecule of nitric acid, HNO_3, $1 + 14 + 48 = 63$. Experiment gives the sp. gr. of nitric acid vapour as 29.6 ($H = 1$), which would give 59.2 as the molecular weight, and this is as near to 63 as would be expected, considering that HNO_3 cannot be vaporised without partial decomposition.

96. *Nitrous oxide* or *laughing gas* ($N_2O = 44$ parts by weight = 2 volumes) is prepared by heating ammonium nitrate, when it is resolved into water and nitrous oxide; $NH_4NO_3 = 2H_2O + N_2O$.

Nitrate of ammonia or ammonium nitrate is obtained by adding fragments of ammonium carbonate to nitric acid * diluted with an equal volume of water, until the carbonate no longer effervesces in the liquid, which is then evaporated down until a drop solidifies on a cold surface, when the whole may be poured out upon a clean stone and the mass broken up and preserved in a well-stoppered bottle, because it is liable to attract moisture from the air. To obtain the nitrous oxide, an ounce of the salt may be gently heated in a small retort, when it melts, boils, and gradually disappears entirely in the forms of steam and nitrous oxide. The latter may be collected with slight loss over water. Crystallised ammonium nitrate may be employed instead of the fused salt.

In the preparation of nitrous oxide, if the temperature be too high, the gas may contain nitric oxide and nitrogen; $NH_4NO_3 = NO + N + 2H_2O$. To purify the gas, it should be passed through a strong solution of ferrous sulphate, to absorb the nitric oxide, and afterwards through potash to absorb acid vapours.

Nitrous oxide is perfectly colourless, but has a slight odour and a sweetish taste. Its characteristic anaesthetic property is well known. It accelerates the combustion of a taper like oxygen itself, and will even kindle into flame a spark at the end of a match. When C is burnt into CO_2 by $2N_2O$, it evolves 40,400 more units of heat than when burnt in O_2, showing that, contrary to the usual law, heat is *evolved* in the *decomposition* of the N_2O, amounting to 20,200 units per molecule. Such a compound is said to be *endothermic*. Nitrous oxide can readily be distinguished from oxygen by shaking it with water, which absorbs, at the ordinary temperature, about three-fourths of its volume of the nitrous oxide. It is absorbed in larger quantity by alcohol. It is also much heavier than oxygen, its specific gravity being 1.53, and is liquefied by a pressure of 40 atmospheres at 45° F., and solidified at −150° F. It is now sold in a liquid state in wrought-iron vessels for use as an anæsthetic in dental surgery.

The liquid nitrous oxide possesses properties similar to those of liquid carbon dioxide with respect to its rapid evaporation; but it may be drawn into test-tubes in a liquid state from the receiver. A lighted match thrown into the liquid burns with great brilliancy. When mixed with carbon disulphide and evaporated *in vacuo*, it produces an extremely low temperature −220° F. (−140° C.).

97. *Nitric oxide* ($NO = 30$ parts by weight = 2 volumes) is usually obtained by the action of copper upon diluted nitric acid (see page 136).

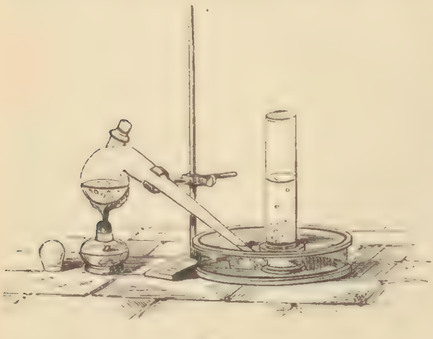

Fig. 154.

300 grains (or 20 grms.) of copper turnings or clippings are introduced into a retort, and 3 measured ounces (or 85 c.c.) of a mixture of concentrated nitric acid with an equal volume of water are poured upon them. A very gentle heat may be applied to assist the action, and the gas may be collected over water (see fig. 154), which absorbs the red fumes (NO_2) formed by the union of the NO with the oxygen of the air contained in the retort.

Nitric oxide is distinguished from all other gases by the production of a red gas, when the colourless nitric oxide is allowed to come in contact with uncombined oxygen, the presence of which, in mixtures of gases, may be readily detected by adding a little nitric oxide. The red gas consists chiefly of nitric peroxide (NO_2) when the oxygen is in excess, otherwise it contains also some nitrous anhydride (N_2O_3).

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* Which must remain clear when tested with silver nitrate, showing it to be free from chlorine.

The combination of nitric oxide with oxygen may be exhibited by decanting a pint bottle of oxygen, under water, into a tall jar filled with water coloured with blue litmus, and adding to it a pint bottle of nitric oxide (fig. 155). Strong red fumes are immediately produced, and on gently agitating the cylinder, the fumes are absorbed by the water, reddening the litmus. The oxygen will now have been reduced to half its volume, and if another pint of nitric oxide be added, the remainder of the oxygen will be absorbed, showing that *two volumes of nitric oxide combine with one volume of oxygen*, forming the nitric peroxide which is absorbed by the water.

In presence of water and excess of oxygen, NO is entirely converted into nitric acid; $2NO + H_2O + O_2 = 2HNO_3$.

The addition of nitric oxide to atmospheric air was one of the earliest methods employed for removing the oxygen in order to determine the composition of air; but important variations were observed in the results, in consequence of the occasional formation of N_2O_3 in addition to the NO_2.

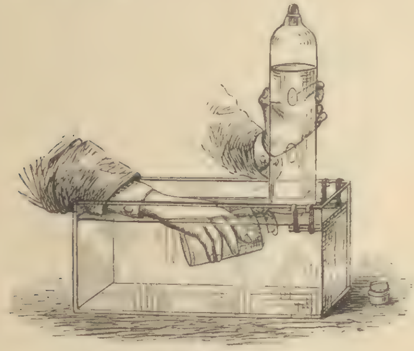

Fig. 155.

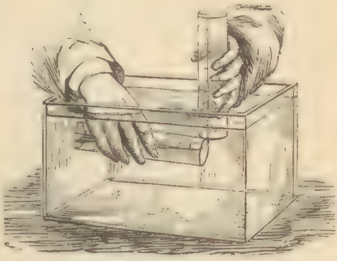

Fig. 156.

The rough analysis of air by this method may be instructively performed with two similar gas cylinders, each divided into ten equal volumes. Into one are introduced five volumes of air, and into the other five volumes of nitric oxide. On decanting the air, under water, into the nitric oxide (fig. 156), the red nitric peroxide will be formed and absorbed by the water, the ten volumes of gas shrinking to seven, showing that three volumes have been absorbed, of which one volume would of course represent the oxygen contained in the five volumes of air.

The nitric oxide prepared by the action of copper on nitric acid generally contains nitrous oxide, and will seldom give correct results in the above experiment. Pure nitric oxide may be obtained by heating in a retort 100 grains (or 6.5 grms.) potassium nitrate, 1000 grains (or 65 grms.) of ferrous sulphate, and three measured ounces (or 85 c.c.) of diluted sulphuric acid (containing one measure of acid to three measures of water), which will yield above two pints (or 1133 c.c.) of gas; $2KNO_3 + 6FeSO_4 + 4H_2SO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$.

In all its properties nitric oxide is very different from nitrous oxide. It is much lighter, having almost exactly the same specific gravity as air, viz., 1.04, and is not dissolved to an important extent by water. It is more difficult to liquefy, requiring a pressure of 104 atmospheres at $-11°$ C. When a lighted taper is immersed in nitric oxide it is extinguished, although this gas contains twice as much oxygen as nitrous oxide, which so much accelerates the combustion of a taper; for the elements are held together by a stronger attraction in the nitric oxide, so that its oxygen is not so readily available for the support of combustion. (The nitric oxide prepared from copper and nitric acid sometimes contains so much nitrous oxide that a taper burns in it brilliantly.) Even phosphorus, when just kindled, is extinguished in nitric oxide, but when allowed to attain to full combustion in air, it burns with extreme brilliancy in the gas. Indeed, nitric oxide appears to be the least easy of decomposition of the whole series of oxides of nitrogen, which accounts for its being the most common result of the decomposition of the other oxides. Nitrous oxide itself, when passed through a red-hot tube, is partly converted into nitric oxide; and when a taper burns in a bottle of nitrous oxide, the upper part of the bottle is often filled with a red gas, indicating the formation of nitric oxide, and its oxidation by the air entering the bottle.

The difference in the stability of the two gases is also shown by their behaviour with hydrogen. A mixture of nitrous oxide with an equal volume of hydrogen explodes when in contact with flame, yielding steam and nitrogen, but a mixture of equal volumes of nitric oxide and hydrogen burns quietly in air, the hydrogen not decomposing the nitric oxide. An excess of hydrogen, however, is capable of decomposing nitric oxide, ammonia and water being formed.

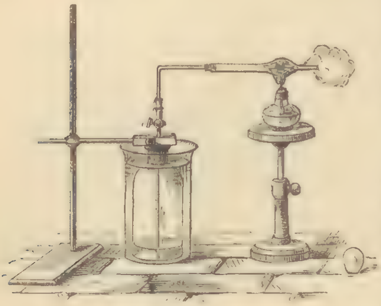
Fig. 157.

If two volumes of nitric oxide be mixed with five volumes of hydrogen and the gas passed through a tube having a bulb filled with platinised asbestos (fig. 157),* the mixture issuing from the orifice of the tube will produce the red vapours by contact with the air, which will strongly redden blue litmus; but if the platinised asbestos be heated with a spirit-lamp, the hydrogen, encouraged by the action of the platinum (90) will decompose the nitric oxide, and strongly alkaline vapours of ammonia will be produced, restoring the blue colour to the reddened litmus; $NO + H_5 = NH_3 + H_2O$. It will be remembered that when oxygen is in excess, ammonia is converted, under the influence of platinum, into water and nitrous acid (90).

Nitric oxide is readily absorbed by ferrous salts, with which it forms dark brown solutions. If a little solution of ferrous sulphate ($FeSO_4$) be shaken in a cylinder of nitric oxide closed with a glass plate, the gas will be immediately absorbed and the solution will become dark brown. On applying heat, the brown compound is decomposed. A compound of $2FeSO_4$ and NO has been obtained in small brown crystals, which lose all their nitric oxide *in vacuo*.

When shaken with moist ferrous hydrate, NO is reduced to N_2O and N. In the presence of caustic soda, sodium hyponitrite (NaNO) and ammonia are also produced. By employing a large excess of soda, one-fifth of the nitric oxide may be converted into the hyponitrite.

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* Asbestos which has been wetted with solution of platinic chloride, dried, and heated to redness, to reduce the platinum to the metallic state.

98. *Nitrous anhydride*, or *nitroso-nitric oxide* ($N_2O_3 = 76$ parts by weight.—Ammonium nitrite is said to exist in minute quantity in rain water, and nitrites are occasionally found in well-waters, where they have probably been formed by the oxidation of ammonia (91). Small quantities of ammonium nitrite appear to be formed by the combustion in air of gases containing hydrogen, this element uniting with the atmospheric oxygen and nitrogen.

Nitrous anhydride may be obtained by heating starch with nitric acid, but the most convenient process consists in gently heating nitric acid (sp. gr. 1.35) with an equal weight of white arsenic, and passing the gas, first through a U-tube (fig. 158) surrounded with cold water, to condense undecomposed nitric acid, then through a similar tube containing calcium chloride, to absorb aqueous vapour, and afterwards into a U-tube surrounded with ice. Through a small tube opening into the bend of this U-tube, the condensed nitrous anhydride drops into a tube drawn out to a narrow neck, so that it may be drawn off, and sealed by the blowpipe—

$$2HNO_3 + \underset{\text{White arsenic.}}{As_2O_3} + 2H_2O = \underset{\text{Arsenic acid.}}{2H_3AsO_4} + N_2O_3.$$

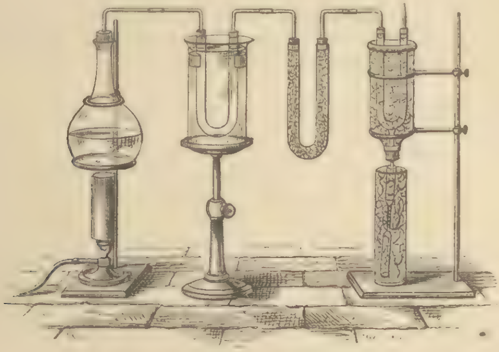

Fig. 158.—Preparation of nitrous anhydride.

Nitrous anhydride is also prepared by decomposing the acid nitrosyle sulphate (see *Aqua regia*) with a small quantity of water—

$$2NOHSO_4 + H_2O = 2H_2SO_4 + N_2O_3.$$

Nitrous anhydride is a green liquid which boils at 14° C., becoming converted into a red vapour, and partly decomposed into NO and NO_2. Water at about 32° F. dissolves the acid without decomposing it, yielding a blue solution, which is decomposed, as the temperature rises, into nitric acid which remains in the liquid, and nitric oxide which escapes with effervescence; $3N_2O_3 + H_2O = 2HNO_3 + 4NO$.

The blue solution is believed to contain *nitrous acid*, HNO_2, resulting from the reaction $N_2O_3 + H_2O = 2HNO_2$; but this compound has not been obtained in a pure state.

A very dilute solution of nitrous acid may be preserved for some time and even distilled without decomposition.

The salts of nitrous acid, or *nitrites*, are interesting on account of their production from the nitrates by the action of heat (p. 139).

If potassium nitrate be fused in a fireclay crucible and heated to redness, it will evolve bubbles of oxygen, and slowly become converted into potassium nitrite (KNO_2) The heat may be continued until a portion removed on the end of an iron rod, and dissolved in water, gives a strongly alkaline solution. The fused mass may then be poured upon a *dry* stone, and, when cool, broken into fragments and preserved in a stoppered bottle. On heating a fragment of the nitrite with diluted sulphuric acid, red vapours will be disengaged, but these contain little nitrous acid, the greater part of this being decomposed by the water into nitric acid and nitric oxide.

When nitrous acid acts upon ammonia, both compounds suffer decomposition, water and nitrogen being the results; $NH_3 + HNO_2 = N_2 + 2H_2O$.

This is sometimes taken advantage of in preparing nitrogen gas by boiling mixed solutions of sal ammoniac and potassium nitrite; $NH_4Cl + KNO_2 = KCl + 2H_2O + N_2$.

In experiments upon organic compounds, nitrous acid is sometimes employed as a convenient agent for effecting simultaneously the removal of 3 atoms of hydrogen from a compound, and the insertion of 1 atom of nitrogen.

When solutions of nitrites are heated in contact with air, they gradually absorb oxygen, becoming converted into nitrates.

Alkali nitrites are reduced, in solution, by ferrous hydrate, yielding N, N_2O, NH_3, and hyponitrites.

When a solution of sodium nitrate, $NaNO_3$, is acted on by sodium amalgam, it is first reduced to sodium nitrite, $NaNO_2$, and then to *sodium hyponitrite*, NaNO, which gives a yellow precipitate of silver hyponitrite, AgNO, on addition of silver nitrate to the solution after neutralisation with nitric acid.* The sodium salt may be prepared in large quantity by fusing sodium nitrate with iron filings in an iron crucible, when the iron abstracts O from the $NaNO_3$, and converts it into NaNO. By boiling the fused mass with water, filtering, and evaporating to a small bulk, needle-shaped crystals are obtained on cooling, which have the formula NaNO.3Aq.

The corresponding acid, HNO, has not been obtained, the attempts to prepare it having resulted in the formation of nitrous oxide and water; $2HNO = N_2O + H_2O$.

99. *Nitric peroxide* ($NO_2 = 46$ parts by weight (or $N_2O_4 = 92$ parts) = 2 volumes), formerly known as *nitrous acid*.—By passing a mixture of nitric oxide with half its volume of oxygen, free from every trace of moisture, into a perfectly dry tube cooled in a mixture of ice and salt, the dark red gas is condensed into colourless prismatic crystals which melt at 10° F. (−12° C.) into a nearly colourless liquid. This gradually becomes yellow as the temperature rises, and at the ordinary temperature has a deep orange colour. It is very volatile, boiling at 71° F. (22° C.), and being converted into a red-brown vapour, which was long mistaken for a permanent gas, on account of the great difficulty of condensing it when once mixed with air or oxygen. Nitric peroxide is also obtained, mixed with one-fourth of its volume of oxygen, by heating lead nitrate (fig. 159); $Pb(NO_3)_2 = PbO + 2NO_2 + O$.

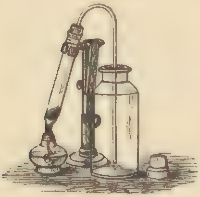

Fig. 159.—Preparation of nitric peroxide.

The vapour of nitric peroxide is much heavier than atmospheric air.

Its specific gravity (compared with hydrogen at the same temperature) diminishes as the temperature rises. At 140° C. it is twenty-three times as heavy as hydrogen, showing its molecular weight to be 46. This variation in density, in conjunction with the other changes with increase of temperature, lead to the belief that the molecule of nitric peroxide at low temperatures (in its liquid state) is N_2O_4, and becomes decomposed into $2NO_2$ at high temperatures. At 500° C. the gas becomes nearly colourless, being almost entirely dissociated into NO, and O.

N_2O_4 is sometimes called *nitrosyle nitrate*, $NO.NO_3$.

Its colour varies with the temperature, becoming very dark at 100° F. The smell of the vapour is very characteristic. It supports the combustion of strongly burning charcoal or phosphorus, and oxidises most of the metals, potassium taking fire in it spontaneously. The nitric peroxide must, therefore, rank as a powerful oxidising agent, and it is the presence of this substance in the red fuming nitric acid that imparts to it higher oxidising powers than those of the colourless nitric acid.

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* Hydroxylamine, $NH_2(OH)$, is formed at the same time.

The so-called *nitrous acid* of commerce is really nitric acid holding in solution a large proportion of nitric peroxide, and is prepared by introducing sulphur into the retorts containing the mixture of sodium nitrate and sulphuric acid employed in the preparation of the nitric acid, a portion of which is de-oxidised and converted into nitric peroxide. Water in excess immediately decomposes the nitric peroxide into nitrous acid and nitric acid; $2NO_2 + H_2O = HNO_3 + HNO_2$.

When water is gradually added to liquid nitric peroxide, it effervesces, from escape of nitric oxide, and becomes green, blue, and ultimately colourless; $3NO_2 + H_2O = NO + 2HNO_3$. If the red nitric acid of commerce be gradually diluted with water, it will be found to undergo similar changes, always becoming colourless at last. The nitric acid which has been used in a Grove's battery always has a green colour, from the large amount of nitric peroxide which has accumulated in it, in consequence of the decomposition of the acid by the hydrogen disengaged during the action of the battery; $H + HNO_3 = H_2O + NO_2$. If this green acid be diluted with a little water it becomes blue, and a larger quantity of water renders it colourless, causing the evolution of nitric oxide. Similar colours are obtained by passing nitric oxide into nitric acid of different degrees of concentration, apparently because nitric peroxide is formed and dissolved by the acid.

When silver, mercury, and some other metals are dissolved in cold nitric acid, a green or blue colour is often produced, leading a novice to suspect the presence of copper, the colour being really caused by the solution, in the unaltered nitric acid, of the nitric peroxide produced by the de-oxidation of another portion.

Nitric peroxide was formerly believed to be an independent acid capable of forming salts. It is true that its vapours have a strongly acid reaction to test-papers, but when brought into contact with alkalies, it produces a mixture of nitrate and nitrite—

$$2NO_2 + 2KHO = KNO_3 + KNO_2 + H_2O.$$

100. *General review of the oxides of nitrogen.*—Nitric oxide, nitrous anhydride, and nitric peroxide are very remarkable for their relations to oxygen. Nitric oxide is one of the very few substances which combine with dry oxygen at the ordinary temperature, and yet the nitric peroxide which is thus produced is very ready to yield its oxygen to other substances. Nitrous anhydride, as might be expected, is intermediate in this respect, being capable of acting as a reducing agent upon powerfully oxidising substances, and as an oxidising agent upon substances having a great attraction for oxygen. Thus a solution of potassium nitrite acidified with sulphuric acid will bleach potassium permanganate, reducing the permanganic acid to manganous oxide (MnO); whilst if added to ferrous sulphate, the nitrite converts the ferrous into ferric salt, and this solution, which was capable of reducing the potassium permanganate before, is now found to be without effect upon it, unless an excess of the nitrite has been added.

The oxides of nitrogen, as illustrating combination in multiple propor-

tions by weight and volume.—In its most general form, the *Law of Multiple Proportions* may be thus stated. When a substance (A) combines with another substance (B) in more than one proportion, the quantities of B which combine with a *constant quantity* of A, are multiples of the smallest combining quantity of B by some whole number.

It was the occurrence of combination in multiple proportions which originally led to the application of the atomic theory to chemistry. Now that chemistry is defined as the science which treats of atoms, the law of multiple proportions follows as a matter of course.

In the oxides of nitrogen this law is exemplified in the simplest form, since the quantities of oxygen which combine with a constant quantity of nitrogen are multiples of the least combining quantity of oxygen by 2, 3, 4, and 5.

		N	O
Nitrous oxide	N_2O	28	16
Nitric oxide (two molecules)	N_2O_2	28	16 × 2
Nitrous anhydride	N_2O_3	28	16 × 3
Nitric peroxide	N_2O_4	28	16 × 4
Nitric anhydride	N_2O_5	28	16 × 5

It was shown at p. 130 that there is ground for representing the atomic weight of nitrogen as = 14.

When *nitrous oxide* is passed through a red-hot porcelain tube, its volume is increased by one-half, and the resulting gas is found to be a mixture of 1 volume of oxygen and 2 volumes of nitrogen. Hence it is inferred that, in nitrous oxide, 2 volumes or atoms (28 parts) of nitrogen are united with 1 volume or atom (16 parts) of oxygen, to form 2 volumes or one molecule of nitrous oxide (representing 44 parts by weight).

When charcoal is strongly heated in *nitric oxide*, the volume of the gas remains unchanged; but it is found on analysis to have become converted into a mixture of equal volumes of carbonic acid gas and nitrogen ($2NO + C = CO_2 + N_2$). Since 1 volume of carbonic acid gas contains 1 volume of oxygen (page 92), the experiment proves that 1 volume of oxygen and 1 volume of nitrogen exist in 2 volumes of nitric oxide, or that 1 atom of nitrogen (or 14 parts) is combined with 1 atom of oxygen (16 parts) in 2 volumes (one molecule, or 30 parts by weight) of nitric oxide.

The direct evidence of the composition of *nitrous anhydride* is not so satisfactory as that in the two preceding cases. This gas has been obtained, however, by the direct union of 1 volume of oxygen with 4 volumes of nitric oxide, leading to the conclusion that it contains N_2O_3.

Nitric peroxide has been analysed by passing the vapour produced from a known weight of the liquid, over red-hot metallic copper, which absorbed the oxygen, leaving the nitrogen to be collected and measured. It was thus found that 14 parts by weight (one atom = 1 volume) of nitrogen were combined with 32 parts by weight (two atoms = 2 volumes) of oxygen, a result which is confirmed by the direct union of 2 volumes of NO (one molecule) with 1 volume of oxygen (one atom) to form NO_2.

Nitric anhydride, or anhydrous nitric acid, was analysed by a method similar to that employed for nitric peroxide, and was found to contain 28 parts by weight (2 atoms) of nitrogen, combined with 80 parts (5 atoms) of oxygen. The volume occupied by the molecule of nitric anhydride in the state of vapour has not been determined, on account of the want of stability of this compound.

The facility with which nitrous anhydride and nitric peroxide can be decomposed with formation of nitric oxide, renders it probable that they really contain that compound. To express this, they may plausibly be represented as formed after the same plan as a molecule of water. Just as in H.O.H, the two atoms of hydrogen are linked together by the diatomic oxygen, so in nitrous anhydride, NO.O.NO, two molecules of nitric oxide are linked together by the atom of oxygen, whilst in nitric peroxide (N_2O_4) a molecule of NO is bound up with a molecule of NO_2, thus, $NO.O.NO_2$. If nitric anhydride be represented by $NO_2.O.NO_2$, it is easy to understand the behaviour of these three oxides with the alkalies. Thus, by the action of nitrous anhydride on caustic potash, we obtain potassium nitrite, K.O.NO, whilst nitric acid gives potassium nitrate, $K.O.NO_2$, and nitric peroxide gives a mixture of both salts.

From the experiments of Berthelot, it appears that the decomposition of all the oxides of nitrogen is attended by evolution of heat, which is greatest for nitric oxide. Hence it would be expected that nitrogen and oxygen would show little disposition to enter into direct combination.

CHLORINE.

Cl = 35.5 parts by weight = 1 volume. 35.5 grs. = 46.7 cub. in. at 60° F. and 30″ Bar. 35.5 grammes = 11.16 litres at 0° C. and 760 mm. Bar.

101. This element is never found in the uncombined state, but is very abundant in the mineral world in the forms of sodium chloride (common salt) and potassium chloride. In these forms also it is an important constituent of the fluids of the animal body, but as it is not found in sufficient proportion in vegetable food, or in the solid parts of animal food, a quantity of salt must be added to these in order to form a wholesome diet. Sodium chloride is indispensable as a raw material for several of the most useful arts, such as the manufactures of soap and glass, bleaching, &c.; in fact, it is the source of three of the most generally useful chemical products—viz., chlorine, hydrochloric acid, and soda.

About the middle of the seventeenth century, a German chemist named Glauber distilled some common salt with sulphuric acid, and obtained a strongly acid liquid to which he gave the name *muriatic acid* (from *muria*, brine), and which was proved to be identical with the acid long known to the alchemists as *spirit of salt* (obtained by distilling salt with clay). The saline mass which was left after the experiment was then termed Glauber's salt, but afterwards received its present name of sodium sulphate.

It was undoubtedly a natural inference from this experiment that common salt was composed of muriatic acid and soda, and that the sulphuric acid had a greater attraction for the soda than the muriatic acid, which was therefore displaced by it. In accordance with this view, common salt was called muriate of soda, without further question, until the year 1810, when the experiments of Davy proved that it was really composed of the two elementary substances, chlorine and sodium, and must therefore be styled, as it now is, sodium chloride, and represented by the formula NaCl. It was further shown by Davy that the muriatic acid was really composed of chlorine and hydrogen, and that it was, in fact, HCl, or chloride of sodium (NaCl), in which the sodium had been displaced by hydrogen.

Preparation of chlorine.—In order to extract chlorine from common salt, it is heated with black oxide of manganese and diluted sulphuric acid, when the sulphates of sodium and manganese are left in solution, and chlorine escapes in the form of gas—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

600 grains (or 40 grms.) of common salt may be mixed with 450 grains (or 30 grms.) of binoxide of manganese, introduced into a retort (fig. 160), and a cold mixture of 1½ oz. (or 42 c.c.) by measure of strong sulphuric acid with 4 oz. (or 110 c.c.) of water poured upon it. The retort having been well shaken, to wet the powder thoroughly with the acid, a very gentle heat is applied, and the gas collected in bottles filled with water and inverted in the pneumatic trough. When the bottles are filled, the stoppers, previously greased, must be inserted into them under water. The first bottle or two will contain the air from the retort, and will therefore have a paler colour than the pure chlorine afterwards

collected. It is advisable to keep a jar filled with water standing ready on the shelf of the trough, so that any excess of chlorine may be passed into it instead of being allowed to escape into the air, causing serious inconvenience. The bottles of moist chlorine must always be preserved in the dark. Chlorine may also be conveniently prepared by gently heating 500 grains (or 30 grms.) of binoxide of manganese with 4 oz. (or 110 c.c.) (measured) of common hydrochloric acid; $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. Either of the above methods will furnish about five pints (or 2800 c.c.) of chlorine. If chlorine be required free from HCl, it may be passed through a strong solution of copper sulphate—

$$CuSO_4 \ + \ 2HCl \ = \ CuCl_2 \ + \ H_2SO_4.$$

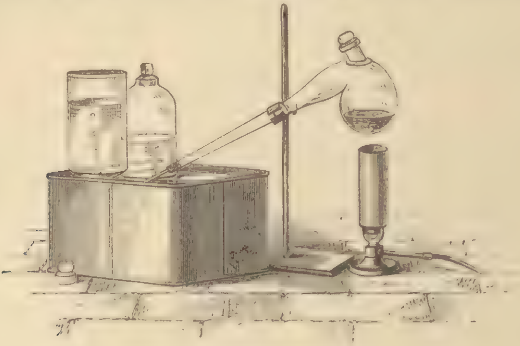

Fig. 160.—Preparation of chlorine.

In *Weldon's process* for the manufacture of chlorine, the manganese is made to act as a carrier of oxygen from the atmosphere to the hydrogen of the hydrochloric acid, setting the chlorine free. For this purpose the chloride of manganese obtained in the above process is decomposed by lime; $MnCl_2 + CaO = CaCl_2 + MnO$. By mixing the MnO with more lime, and blowing atmospheric air through the mixture, MnO_2 is reproduced, and may be employed for decomposing a fresh quantity of HCl. In *Deacon's process*, a mixture of air and hydrochloric acid gas is passed over heated fire-brick which has been soaked in solution of copper sulphate and sodium sulphate, and dried. The final result is expressed by the equation $2HCl + (N_4 + O) = H_2O + Cl_2 + N_4$, so that the chlorine obtained is mixed with twice its volume of nitrogen, which is stated, however, not to interfere seriously with its useful application. The action of the copper-salt has not been clearly explained, but it appears to depend upon the instability of the chlorides of copper under the influence of heat and oxygen.

Properties of chlorine.—The physical and chemical properties of chlorine are more striking than those of any element hitherto considered. Its colour, whence it derives its name (χλωρός, pale green), is bright greenish-yellow, its odour insupportable. It is twice and a half as heavy as air (sp. gr. 2.47), and may be reduced to the liquid state by cooling it to − 34° C., or by a pressure of 8.5 atmospheres at 12°.5 C. If a bottle of chlorine be held mouth downwards in water, its stopper removed, one-third of the chlorine decanted into a jar, and the rest of the gas shaken with the water in the bottle, the mouth of which is closed by the palm of the hand (fig. 161), the water will absorb nearly twice its volume of chlorine, producing a partial vacuum in the bottle, which will be held firmly against the hand by atmospheric pressure. If air be then allowed to enter, and the bottle again shaken

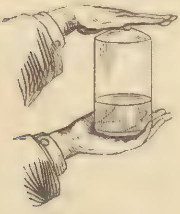

Fig. 161.

as long as any absorption takes place, a saturated solution of chlorine (*liquor chlori, chlorine water*) will be obtained. By exposing this yellow solution to a temperature approaching 32° F., yellow crystals of *hydrate of chlorine** ($Cl.5H_2O$) are obtained, the liquid becoming colourless.

When the water in the pneumatic trough, over which chlorine is being collected, happens to be very cold, the gas is often so foggy as to be quite opaque, in consequence of the deposition of minute crystals of the hydrate. On standing, the gas becomes clear, crystals of the hydrate being deposited like hoar-frost upon the sides of the bottle; the gas also becomes clear when the bottles are slightly warmed.

The hydrate of chlorine affords a convenient source of liquid chlorine. A number of bottles of saturated solution of chlorine, prepared as above, are exposed on a cold winter's day until the hydrate has crystallised. The crystals are thrown upon a filter cooled to nearly 32°, allowed to drain, and rammed into a pretty strong tube closed at one end, about 12 inches long, and ½ an inch in diameter, previously cooled in ice or snow. The tube, having been nearly filled with the crystals, is kept surrounded with snow, whilst its upper end is gradually softened in the blowpipe flame and drawn off so as to be strongly sealed. When this tube is immersed in water at 100° F. (38° C.), the chlorine separates from the water, and two layers of liquid are formed, the lower one consisting of amber-yellow liquid chlorine (sp. gr. 1.33), and the upper of a pale yellow aqueous solution of chlorine. On allowing the tube to cool again, the crystalline hydrate is reproduced, even at common temperatures, being more permanent under pressure. It may even be sublimed in a sealed tube.

Liquid chlorine may also be obtained in a state in which it can be preserved, by disengaging the chlorine in a sealed tube (as in the liquefaction of ammonia) from about 200 grains of platinic chloride previously dried at 400° F. The chloride is heated with a spirit-lamp in one limb of the tube, whilst the other is immersed in a freezing mixture. The face and hands of the operator should be protected against the bursting of the tube.

The most characteristic chemical feature of chlorine is its powerful attraction for many other elements at the ordinary temperature. Among the non-metals, hydrogen, bromine, iodine, sulphur, selenium, phosphorus, and arsenic combine spontaneously with chlorine, and nearly all the metals behave in the same way.†

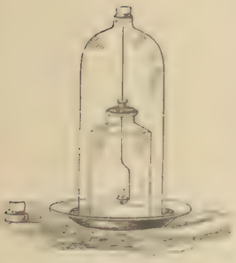

Fig. 162.

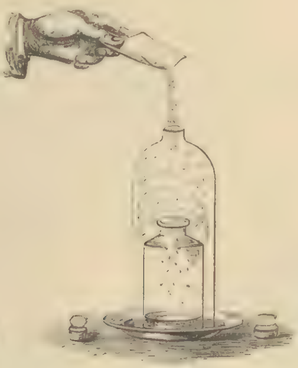

Fig. 163.

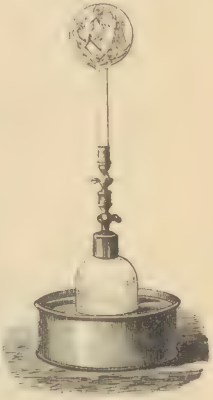

Fig. 164.

If a piece of dry phosphorus be placed in a deflagrating spoon, and immersed in a bottle of chlorine (fig. 162), it will take fire spontaneously, combining with the chlorine to form phosphorous chloride (PCl_3). A tall glass shade may be placed over the bottle, which should stand in a plate containing water, so that the fumes may not escape into the air.

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* According to the modern definition, this is not a *hydrate* but a *combination with water*, or *aquate*.

† The remarkable observation has been made that sodium may be fused in *absolutely dry* chlorine gas without alteration, while in ordinary chlorine violent combustion occurs.

If phosphorus be placed in a bottle of oxygen to which a small quantity of chlorine has been added, it will burst out after a minute or two into most brilliant combustion.

Powdered antimony (the metal, not the sulphide), sprinkled into a bottle of chlorine (fig. 163), descends in a brilliant shower of white sparks, the antimony burning in the chlorine to form antimonious chloride ($SbCl_3$). A little water should be placed at the bottom of the bottle to prevent it from being cracked, and the fumes should be restrained by a shade standing in water.

If a flask, provided with a stopcock (fig. 164), be filled with leaves of *Dutch metal* (an alloy of copper and zinc resembling gold leaf), exhausted of air, and screwed on to a capped jar of chlorine standing over water, it will be found, on opening the stopcocks so that the chlorine may enter the flask, that the metal burns with a red light, forming thick yellow fumes containing cupric chloride ($CuCl_2$) and zinc chloride ($ZnCl_2$). If a gold leaf be suspended in chlorine, it will not be immediately attacked, but will gradually become converted into auric chloride ($AuCl_3$).

102. The most important useful applications of chlorine depend upon its powerful chemical attraction for hydrogen. The two gases may be mixed without combining, if kept in the dark; but when the mixture is exposed to light, they combine to form hydrochloric acid gas (HCl), with a rapidity proportionate to the intensity of the *actinic* rays (or rays capable of inducing chemical change) in the light employed. Exposed to gas-light or ordinary diffused daylight, the hydrogen and chlorine combine slowly; but direct sunlight causes sudden combination, attended with explosion, resulting from the expansion which the hydrochloric acid formed suffers by the heat evolved in the act of combination. The light of magnesium burning in air, and some other artificial lights, also cause sudden combination.

Two pint gas-bottles should be ground so that their mouths may be fitted accurately to each other, and filled respectively with dry hydrogen and dry chlorine, both gases having been dried by passing through oil of vitriol, and collected, the hydrogen by upward, and the chlorine by downward, displacement of air. The mouths should be slightly greased before the bottles are filled with gas, and afterwards closed with glass plates. On placing the bottles together, and removing the plates so that the gases may come in contact (see fig. 146), the yellow colour of the chlorine will be permanent as long as the mixture is kept in the dark, but on exposure to daylight the colour will gradually disappear, the hydrochloric acid gas being colourless. If the bottles be now closed with glass plates, the small quantity of gas which escapes during the operation will be seen to fume strongly in air, a property not possessed either by hydrogen or chlorine; and when the necks of the bottles are immersed in water, and the glass plates withdrawn, the water will gradually absorb the gas, and be forced into the bottles so as to fill them, with the exception of a small space occupied by the air accidentally admitted, showing that the hydrochloric acid gas possesses the joint volumes of the hydrogen and chlorine. If the water be tinged with blue litmus, it will be strongly reddened as it enters the bottles.

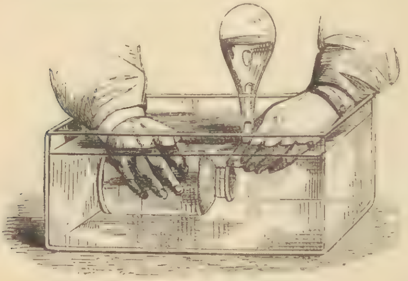
Fig. 165.

The sudden union of the gases with explosion may be safely exhibited in a Florence flask. The flask is filled with water, which is then poured out into a measure. Exactly half the water is returned to the flask, and its level in the latter carefully marked with a diamond or file. The flask, having been again filled with water, is closed with the thumb and inverted in the pneumatic trough, so that hydrogen may be passed up into it to displace one-half of the water. A short-necked funnel is then inserted, under the water, into the neck of the flask, and chlorine rapidly decanted up from a gas-bottle (fig. 165) until the rest of the water has been displaced. The flask is now raised from the water and quickly closed with a cork (fig. 166), through which pass two gutta-percha-covered copper wires, the ends of which have been stripped and brought sufficiently near to each other to allow of the passage of the electric spark within the flask. The ends external to the flask are also stripped and bent into hooks, for convenient connexion with the conducting wires. The flask is placed upon the ground, and covered with a wooden box to prevent the pieces from flying about. On connecting the copper wires with the conducting wires from an induction-coil or an electrical machine, it will be heard, on passing the spark, that the mixture has violently exploded; on raising the box, it will be found filled with strong fumes of hydrochloric acid, and a heap of small fragments of glass will represent the flask.

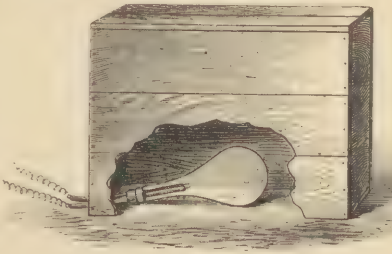

Fig. 166.

A flask filled in the same way with the mixture of hydrogen and chlorine may be attached to the end of a long stick, and thrust out into the sunlight, when it explodes with great violence.

To illustrate the direct combination of hydrogen and chlorine under the influence of artificial light, a strong half-pint gas cylinder is half filled with hydrogen, over water, then filled up quickly with chlorine, also over water, closed with a thin plate of mica, placed mouth upwards on the table, and a piece of burning magnesium tape held close to the side of the cylinder; the lightness of the mica plate obviates any danger.

The attraction of chlorine for hydrogen enables it to effect the decomposition of water. The solution of chlorine in water may be preserved in the dark without change; but when exposed to light, it loses the smell of chlorine and becomes converted into weak hydrochloric

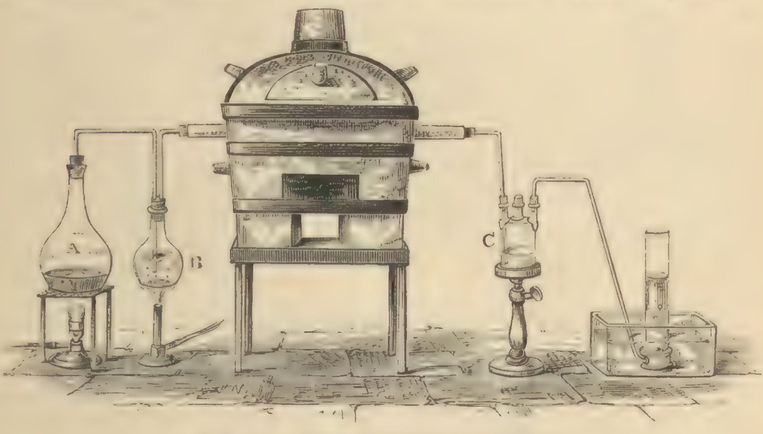

Fig. 167.—Steam decomposed by chlorine.

acid, the oxygen being liberated; $H_2O + Cl_2 = 2HCl + O$.* The decomposition takes place much more quickly at a red heat, so that oxygen is obtained in abundance by passing a mixture of chlorine and steam through a red-hot tube.

For this experiment a porcelain tube is employed, which is loosely filled with fragments of broken porcelain, to expose a large heated surface. This tube is gradually heated to redness in a charcoal furnace (fig. 167). One end of it receives the mixture of chlorine with steam, obtained by passing the chlorine evolved from hydrochloric acid and manganese dioxide in A, through a flask (B) of boiling water. The other end of the tube is connected with a bottle (C) containing solution of potash, to absorb any excess of chlorine and the hydrochloric acid formed; from this bottle the oxygen is collected over the pneumatic trough.

Since water is decomposed by chlorine, it is not surprising that most other hydrogen compounds are attacked by it. Ammonia (NH_3) is acted on with great violence. If a stream of ammonia gas issuing from a tube connected with a flask in which solution of ammonia is heated (see fig. 144) be passed into a bottle of chlorine, it takes fire immediately, burning with a peculiar flame, and yielding thick white clouds of ammonium chloride; $4NH_3 + Cl_3 = 3NH_4Cl + N$. A piece of folded filter-paper dipped in strong ammonia, and immersed in a bottle of chlorine, will exhibit the same effect. When the chlorine is allowed to act upon ammonium chloride, its operation is less violent, and one of the most explosive substances is produced, which was formerly believed to be a *chloride of nitrogen*, but is probably a compound formed by the removal of a part of the hydrogen from ammonia, and the introduction of chlorine in its stead.

Many of the compounds of hydrogen with carbon are also decomposed with violence by chlorine. When a piece of folded filter-paper is dipped into oil of turpentine ($C_{10}H_{16}$), and afterwards into a bottle of chlorine, it bursts into a red flame, liberating voluminous clouds of carbon and hydrochloric acid. Acetylene (C_2H_2) was found to explode spontaneously with chlorine when exposed to light (page 94). The striking decomposition of olefiant gas (C_2H_4) by chlorine on the approach of a flame has already been noticed (page 97). When a lighted taper is immersed in pure chlorine, it is extinguished; but if a little air be present, it continues to burn with a small red flame, the hydrogen only of the wax combining with the chlorine, whilst the carbon separates in black smoke, mixed with the hydrochloric fumes. A mixture of chlorine with an equal volume of oxygen burns up much of the carbon, with a very pretty effect. When chlorine is brought in contact with the flame of a spirit-lamp, it renders the flame luminous by causing the separation of solid particles of carbon (page 104). It has been seen, in the case of olefiant gas, that chlorine sometimes combines directly with the hydrocarbons.

When marsh gas (CH_4) is diluted with an equal bulk of carbon dioxide to prevent violent action, and 4 volumes of chlorine are added for each volume of marsh gas, an oily mixture is gradually formed under the influence of daylight. This oily liquid is a mixture of chloroform and carbon tetrachloride, the production of which is explained by the following equations:—

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* A portion of this oxygen becomes hypochlorous acid, $HClO$, and perchloric acid, $HClO_4$.

$$CH_4 + Cl_6 = 3HCl + CHCl_3 \text{ (Chloroform).}$$
$$CH_4 + Cl_8 = 4HCl + CCl_4 \text{ (Carbon tetrachloride).}$$

It is evident from these equations that chlorine is capable, not only of removing hydrogen from a compound, but also of taking its place, atom for atom—a mode of action which gives rise to a very large number of chlorinated products from organic substances.

The attraction of chlorine for hydrogen enables the moist gas to act as an oxidising agent. Thus, if marsh gas and chlorine be mixed in the presence of water, and exposed to daylight, the water is decomposed, its hydrogen combining with the chlorine, and its oxygen with the carbon of the marsh gas; $CH_4 + 2H_2O + Cl_8 = CO_2 + 8HCl$.

103. The powerful bleaching effect of chlorine upon organic colouring matters is now easily understood. If a solution of chlorine in water be poured into solution of indigo (*sulphindigotic acid*), the blue colour of the indigo is discharged, and gives place to a comparatively light yellow colour. The presence of water is essential to the bleaching of indigo by chlorine, the dry gas not affecting the colour of dry indigo. The indigo is first oxidised at the expense of the water and converted into *isatine*, which is then acted upon by the chlorine and converted into *chlorisatine*, having a brownish-yellow colour—

$$C_{16}H_{10}N_2O_2 \text{ (Indigo)} + 2H_2O + Cl_4 = 2C_8H_5NO_2 \text{ (Isatine)} + 4HCl$$
$$C_8H_5NO_2 \text{ (Isatine)} + Cl_2 = C_8H_4ClNO_2 \text{ (Chlorisatine)} + HCl.$$

Nearly all vegetable and animal colouring matters contain carbon, hydrogen, nitrogen, and oxygen, and are converted by moist chlorine into products of oxidation or chlorination which happen to be colourless, or nearly so.

That dry chlorine will not bleach may be shown by shaking some oil of vitriol in a bottle of the gas and allowing it to stand for an hour or two, so that the acid may remove the whole of the moisture. If a piece of crimson paper be dried at a moderate heat and suspended in the bottle while warm, it will remain unbleached for hours; but a similar piece of paper suspended in a bottle of moist chlorine will be bleached almost immediately. If characters be written on crimson paper with a wet brush, and the paper placed in a jar beside a bottle of chlorine (fig. 168), it will be found on removing the stopper that white characters soon make their appearance on the red ground.

If a collection of coloured linen or cotton fabrics, or of artificial flowers, be exposed to the action of moist chlorine gas or of chlorine water, those which are dyed with organic colouring matters will be bleached at once, whilst the mineral colours will for the most part remain unaltered. Green leaves immersed in chlorine acquire a rich autumnal brown tint, and are eventually bleached. All flowers are very readily bleached by this gas.

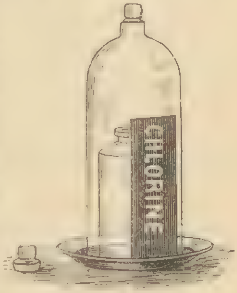

Fig. 168.

Chlorine is very extensively employed for bleaching linen and cotton, the gas acting upon the colouring matter without affecting the fibre; but silk and wool present much less resistance to chemical action, and would be much injured by chlorine, so that they are always bleached by sulphurous acid gas.

Neither chlorine itself nor its solution in water can be very conveniently employed for bleaching on the large scale, on account of the irritating effect of the gas, so that it is usual to employ it in the form of *chloride of lime*, from which it can be easily liberated as it is wanted.

104. The explanation above given of the bleaching effect of chlorine may probably be applied also to its so-called *disinfecting* properties. The atmosphere, in particular localities, is occasionally contaminated with poisonous substances, some of which are known only by their injurious effects upon the health, their quantity being so small that they do not appear in the results of the analysis of such air. Since, however, these substances appear to be acted upon by the same agents which are usually found to decompose organic compounds, they are commonly believed to be bodies of this class, and chlorine has been very commonly employed to combat these insidious enemies to health, since Guyton de Morveau, in the latter part of the last century, made use of it to destroy the odour arising from the bodies interred in the vaults beneath the cathedral of Dijon.

Among the offensive and unhealthy products of putrefaction of animal and vegetable matter, sulphuretted hydrogen, ammonia, and bodies similarly constituted are found. That chlorine breaks up these hydrogen compounds is well known, and hence its great value for removing the unwholesome properties of the air in badly drained houses, &c.

105. The discovery of chlorine, and the discussions which ensued with respect to its real nature, contributed very largely to the advancement of chemical science. About the year 1770, the Swedish chemist Scheele (who afterwards discovered oxygen) first obtained chlorine by heating manganese ore with muriatic acid.

The construction which Scheele put upon the result of this experiment was one which was consistent with the chemistry of that date. He supposed the muriatic acid to have been deprived of *phlogiston*, and hence chlorine was termed by him *dephlogisticated muriatic acid*. This phlogiston had long been a subject of contention among philosophers, having been originally assumed to exist in combination with all combustible bodies, and to be separated from them during their combustion. Towards the decline of the phlogistic theory, attempts were made to prove the identity of this imaginary substance with hydrogen, which shows how very nearly Scheele's reasoning approached to the truth, even with the very imperfect light which he then possessed. Berthollet's movement was retrograde when, ten years afterwards, he styled chlorine *oxygenised muriatic* or *oxymuriatic acid ;* but the experiments of Gay-Lussac and Thénard, and more particularly those of Davy in 1811, proved decisively that hydrochloric acid was composed of chlorine and hydrogen, and that the effect of the black oxide of manganese in Scheele's experiment was to remove the hydrogen in the form of water, thus setting the chlorine at liberty.

HYDROCHLORIC ACID, OR HYDRIC CHLORIDE.

$HCl = 36.5$ parts by weight = 2 volumes.

106. This acid is found in nature among the gases emanating from active volcanoes, and occasionally in the spring and river waters of volcanic districts. For use it is always prepared artificially by the action of sulphuric acid upon common salt—

$$\underset{\text{Common salt}}{NaCl} + H_2SO_4 = HCl + \underset{\text{Hydro-sodium sulphate}}{NaHSO_4}$$

—the sodium of the common salt changing places with the hydrogen of the sulphuric acid.

300 grains (or 20 grms.) of common salt (previously dried in an oven) are introduced into a dry Florence flask (fig. 169), to which has been fitted, by means of a perforated cork, a tube bent twice at right angles, to allow the gas to be collected by downward displacement. Six fluid drachms (or 30 c.c.) of strong sulphuric acid are poured upon the salt, and, the cork having been inserted, the flask is very gently heated, in order to promote the disengagement of the hydrochloric acid gas, which is collected in a perfectly dry bottle, the mouth of which, when full, may be covered with a glass plate smeared with a little grease. While being filled, the bottle may be closed with a perforated card.

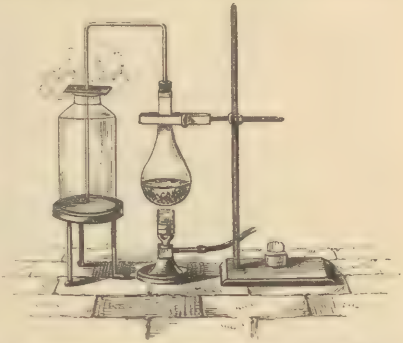
Fig 169.—Preparation of hydrochloric acid gas.

Common salt in powder sometimes froths to a very inconvenient extent with sulphuric acid; it is therefore often preferable to employ fragments of rock salt or of fused salt, prepared by fusing the common salt in a clay crucible, and pouring on to a clean dry stone.

A very regular supply of hydrochloric acid gas is obtained from 1½ oz. of sal ammoniac in lumps, and 1¼ oz. (measured) of sulphuric acid.

The bottle will be known to be filled with gas by the abundant escape of the dense fumes which hydrochloric acid gas, itself transparent, produces by condensing the moisture of the air; for since the gas is much heavier than air (sp. gr. 1.278), it will not escape in any quantity from the bottle until the latter is full. The odour of the gas is very suffocating, but not nearly so irritating as that of chlorine. The powerful attraction for water is one of the most important properties of hydrochloric acid gas.

If a jar of hydrochloric acid gas be closed with a glass plate and inverted under water, it will be found on removing the plate that the gas is absorbed with great rapidity, the water being forced up into the bottle by the pressure of the external air in proportion as the gas is absorbed.

A Florence flask is more convenient than a gas-bottle for this experiment. It must be perfectly dry, and thoroughly well filled with the gas, which may be allowed to escape abundantly from the mouth. The tube delivering the hydrochloric acid gas must be slowly withdrawn, so that the vacancy may be filled by gas, and not by air. The flask is then closed with the thumb, and opened under water, which will enter it with great violence. The experiment may also be made as in the case of ammonia (fig. 170, see page 125).

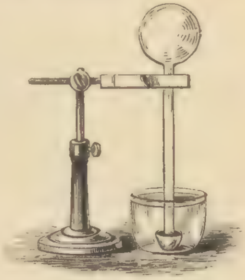
Fig. 170.

Hydrochloric acid liquefies at – 102° C. and solidifies at – 116° C.

The liquid hydrochloric, or *muriatic acid* of commerce, is a solution of the gas in water, and may be recognised by the grey fumes, with the peculiar odour of the acid, which it evolves when exposed to the air. One pint of water at a temperature of 40° F. is capable of absorbing

480 pints of hydrochloric acid gas, forming $1\frac{1}{3}$ pint of the solution, having the specific gravity 1.21. The strength of the acid purchased in commerce is usually inferred from the specific gravity, by reference to tables indicating the weight of hydrochloric acid contained in solutions of different specific gravities. The strongest hydrochloric acid (sp. gr. 1.21) contains 43 per cent. by weight of the gas. At − 18° C. it deposits crystals of $HCl.4Aq$. The common acid has usually a bright yellow colour, due to the accidental presence of a little ferric chloride (Fe_2Cl_6).

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid in order to convert it into sodium sulphate, as a preliminary step to the production of sodium carbonate. The alkali manufacturer is compelled to condense the gas, for it is found to wither up the vegetation in the neighbourhood. For this purpose the hydrochloric acid gas is drawn up from the furnace through vertical cylinders filled with coke, over which streams of water are made to trickle. The water absorbs the acid, and is drawn off from below.

In preparing a pure solution of the acid for chemical use on a small scale, the gas prepared as above may be passed into a small bottle containing a very little water, to wash the gas, or remove any sodium sulphate which may splash over, and then into a bottle about two-thirds filled with distilled water, the tube delivering the gas passing only about $\frac{1}{10}$ inch below the surface, so that the heavy solution of hydrochloric acid may fall to the bottom, and fresh water may be presented to the gas (fig. 171). For ordinary use, an acid of suitable strength is obtained by passing the gas from 6 ounces (170 grms.) of common salt and 10 ounces (or 280 c.c.) of sulphuric acid into 7 (measured) ounces (or 200 c.c.) of water until its bulk has increased to 8 ounces. The bottle containing the water should be surrounded with cold water, since the absorption of hydrochloric acid by water is attended with evolution of heat.

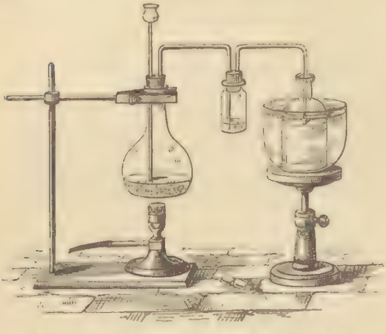

Fig. 171.—Preparation of solution of hydrochloric acid.

Pure solution of hydrochloric acid is sometimes prepared on the large scale by allowing concentrated sulphuric acid to run into the common hydrochloric acid, when the gas is evolved, which is washed and passed into water.

When the concentrated solution of hydrochloric acid is heated in a retort it evolves abundance of hydrochloric acid gas, rendering it probable that it is not a true chemical compound of water with the acid. The evolution of gas ceases when the remaining liquid contains 20 per cent. of acid (and has a sp. gr. of 1.10). If a weaker acid than this be heated, it loses water until it has attained this strength, when it distils unchanged at 110° C.*

The concentrated solution forms a very convenient source from which to procure the gas. It may be heated in a flask, and the gas dried by passing through a bottle filled with fragments of pumice-stone wetted with concentrated sulphuric acid, being collected over the mercurial trough (fig. 172).

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* The proportion of acid thus retained by the water varies directly with the atmospheric pressure to which it is exposed during the distillation.

The avidity with which water absorbs hydrochloric acid is the more remarkable, because this gas can be liquefied only under a very high pressure, amounting at the ordinary temperature to about 40 atmospheres.

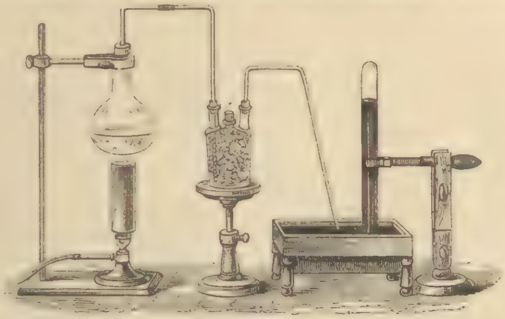

Fig. 172.

The liquefied hydrochloric acid has comparatively little action even upon those metals which decompose its aqueous solution with great violence; quicklime is unaffected by it, and solid litmus dissolves in it with a faint purple colour, instead of the bright red imparted by the aqueous hydrochloric acid. Dry hydrochloric acid gas is not absorbed by calcium carbonate.

The injurious action of hydrochloric acid gas upon growing plants is probably connected with its attraction for water. If a spray of fresh leaves is placed in a bottle of hydrochloric acid, it becomes at once brown and shrivelled.

107. *Action of hydrochloric acid upon metals.*—Those metals which have the strongest attraction for oxygen will also generally have the strongest attraction for chlorine, so that in respect to their capability of decomposing hydrochloric acid, they may be ranked in pretty nearly the same order as in their action upon water (p. 13). Since, however, the attraction of chlorine for the metals is generally superior to that of oxygen, the metals are more easily acted upon by hydrochloric acid than by water, the metal taking the place of the hydrogen, and a chloride of the metal being formed.

Even silver, which does not decompose water at any temperature, is dissolved, though very slowly, by boiling concentrated hydrochloric acid, the chloride of silver formed being soluble in the strong acid, though it may be precipitated by adding water.

Gold and platinum, however, are not attacked by hydrochloric acid; but if a little free chlorine be present, it converts them into chlorides.

Iron and zinc decompose the acid very rapidly in the cold, forming ferrous chloride and zinc chloride, and liberating hydrogen; $Fe + 2HCl = FeCl_2 + H_2$.

When potassium or sodium is exposed to hydrochloric acid gas, it immediately becomes coated with a white crust of chloride, which partly protects the metal from the action of the gas; but when these metals are heated to fusion in hydrochloric acid gas, they burn vividly; $Na + HCl = NaCl + H$.

The composition of hydrochloric acid may be exhibited by confining a measured volume of the gas over mercury (see fig. 82, p. 86), and passing up a freshly cut pellet of sodium. On gently agitating the tube, the gas diminishes in volume, and after a time will have contracted to one-half, and will be found to have all the properties of hydrogen. This result confirms that obtained by synthesis, as described above, that 2 volumes of hydrochloric acid contain 1 volume of hydrogen and 1 volume of chlorine.

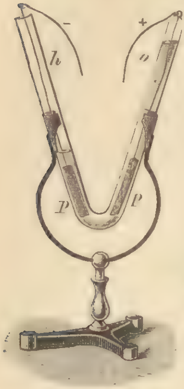

Fig. 173.

The electrolysis of hydrochloric acid is exhibited in the V-tube represented in fig. 173, where the platinum plate *p* in the closed limb *o* is connected with a platinum wire sealed into the glass; the other limb *h* is open. If the closed limb be entirely filled with strong hydrochloric acid, and connected with the negative pole of a battery composed of five or six Grove's or Bunsen's cells, the positive pole being connected with *h*, hydrogen will rapidly collect in the closed limb, whilst the odour of chlorine will be perceived in the open limb. As soon as the liquid fills the open limb, the wire *h* is withdrawn, this limb closed with the thumb, and the hydrogen transferred to it by inclining the tube. After testing the hydrogen with a match, the poles of the battery may be reversed, when the chlorine will collect as gas in the closed limb, as soon as the hydrochloric acid has become saturated with it.

108. *Action of hydrochloric acid upon metallic oxides.*—As a general rule, it may be stated that, when hydrochloric acid acts upon the oxide of a metal, the results are water and a chloride of the metal, in which each atom of oxygen in the oxide has been displaced by 2 atoms of chlorine.

Thus, silver oxide acted on by hydrochloric acid gas gives water and silver chloride; $Ag_2O + 2HCl = H_2O + 2AgCl$.

Suboxide of copper (cuprous oxide) yields water and subchloride of copper (cuprous chloride); $Cu_2O + 2HCl = H_2O + Cu_2Cl_2$.

Ferric oxide gives water and ferric chloride; $Fe_2O_3 + 6HCl = 3H_2O + Fe_2Cl_6$.

With stannic oxide, water and stannic chloride are obtained; $SnO_2 + 4HCl = 2H_2O + SnCl_4$.

Antimonious oxide is converted into water and antimonious chloride; $Sb_2O_3 + 6HCl = 3H_2O + 2SbCl_3$.

109. In cases where the corresponding chloride does not exist, or is not stable under the conditions of the experiment, a chloride is formed containing less chlorine than is equivalent to the oxygen in the oxide, and the balance is evolved in the free state. Thus, when manganese sesquioxide and dioxide are heated with hydrochloric acid—

$$Mn_2O_3 + 6HCl = 3H_2O + 2MnCl_2 + Cl_2;$$
$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

Chromic anhydride, a chloride corresponding to which is not known to exist, when heated with hydrochloric acid, yields chromic chloride and chlorine; $2CrO_3 + 12HCl = 6H_2O + Cr_2Cl_6 + Cl_6$.

Most metallic oxides containing 1 atom of oxygen have a corresponding chloride of a stable character, but the higher oxides less frequently form corresponding chlorides endowed with any stability. *Basic oxides* rarely evolve chlorine from hydrochloric acid. When an oxide gives off chlorine on boiling with hydrochloric acid it is probably a *peroxide* or an *acid oxide*.

Compounds of Chlorine with Oxygen.

110. It is worthy of notice, that whilst chlorine and hydrogen so readily unite, there is no method by which chlorine can be made to combine in a direct manner with oxygen, the compounds of these elements having been hitherto obtained only by indirect processes. An excellent illustration is thus afforded of the fact, that the more closely substances resemble each other in their chemical relations, the less will be their tendency to combine; for chlorine and oxygen are both highly electro-negative bodies, and therefore, having both a powerful attraction for the electro-positive hydrogen, their attraction for each other is of a very low order.

Two oxides of chlorine are known, Cl_2O and ClO_2.

111. *Hypochlorous anhydride*, or *chlorous oxide* (Cl_2O), is of some practical interest in connexion with *chloride of lime*, *chloride of soda*, and other bleaching compounds. It is prepared by passing dry chlorine gas over dry precipitated mercuric oxide, and condensing the product in a tube surrounded with a mixture of ice and salt; $HgO + Cl_4 = HgCl_2 + Cl_2O$.

The hypochlorous anhydride is thus obtained as a deep red liquid, which boils at 19° C. (66° F.), evolving a yellow vapour twice as heavy as air, and having a very powerful and peculiar odour. This vapour is remarkably explosive, the heat of the hand having been known to cause its separation into its constituents, when 2 volumes of the vapour yield 2 volumes of chlorine and 1 volume of oxygen. As might be expected, most substances which have any attraction for oxygen or chlorine will decompose the gas, sometimes with explosive violence. Even hydrochloric acid decomposes it: 1 volume of chlorous oxide is entirely decomposed by 2 volumes of hydrochloric acid, yielding water and chlorine; $Cl_2O + 2HCl = H_2O + Cl_4$. Chlorous oxide is a powerful bleaching agent, both its chlorine and oxygen acting upon the colouring matter in the manner explained at page 153.

Hypochlorous anhydride is absorbed in large quantity by water; the solution is supposed to contain *hypochlorous acid*, HClO, for $H_2O + Cl_2O = 2HClO$; but HClO has not been obtained in the separate state. The solution may be very readily prepared by shaking mercuric oxide with water in a bottle of chlorine as long as the gas is absorbed. The greater part of the mercuric chloride which is produced combines with the excess of oxide to form a brown insoluble oxychloride, whilst the hypochlorous acid and a little mercuric chloride remain in solution. This solution is a most powerful oxidising and bleaching agent; it erases writing ink immediately, and does not corrode the paper if it be carefully washed. Printing ink, which contains lamp black and grease, is not bleached by hypochlorous acid, so that this solution is very useful for removing ink stains from books, engravings, &c.

The action of some metals and their oxides upon solution of hypochlorous acid is instructive. Iron seizes upon the oxygen, whilst the chlorine is liberated; copper takes both the oxygen and chlorine; whilst silver combines with the chlorine, and liberates oxygen. Mercury yields, on shaking, the brown mercuric oxychloride. This distinguishes solution of HClO from chlorine water. Oxide of lead (PbO) removes the oxygen, becoming peroxide of lead (PbO_2), and liberating chlorine, but oxide of silver converts the chlorine into chloride of silver, and liberates the oxygen; $Ag_2O + Cl_2O = 2AgCl + O_2$.

Hypochlorous acid is formed when a weak solution of hydric peroxide is added to a large excess of chlorine water; $Cl_2 + H_2O_2 = 2HClO$. With an excess of the peroxide, $HClO + H_2O_2 = HCl + H_2O + O_2$.

The salts of hypochlorous acid, or *hypochlorites*, are not known in a pure state, but are obtained in solution by neutralising hypochlorous acid with bases.* They are decomposed even by carbonic acid, with liberation of hypochlorous acid.

When the solution of a hypochlorite is boiled, it becomes converted into a mixture of chloride and chlorate; $3KClO = KClO_3 + 2KCl$. This change is turned to practical account in the manufacture of potassium chlorate. It is much hindered by the presence of an excess of alkali. The solution of hypochlorous acid itself, when exposed to light, is decomposed into chloric acid and free chlorine; $5HClO = HClO_3 + 2H_2O + Cl_4$.

A solution of hypochlorous acid may be obtained by adding boric acid in excess to a solution of chloride of lime.

112. *Chloride of lime*, or *bleaching powder*, or *calx chlorata*, is prepared by passing chlorine gas into boxes of lead or stone in which a quantity of moist slaked lime is spread out upon shelves. The temperature is not allowed to rise above 25° C. (77° F.), which is ensured by acting upon the fresh lime with chlorine diluted by air. The lime absorbs nearly half its weight of chlorine, and forms a white powder, which has a very peculiar smell, somewhat different from that of chlorine.

The formula of chloride of lime is generally written CaCl.OCl.

The constitution of chloride of lime appears doubtful. When the calcium hydrate, $Ca(HO)_2$, is acted on by chlorine, the simplest reaction would be $Ca(HO)_2 + Cl_2 = CaCl(ClO) + H_2O$, according to which the chloride of lime would result from the replacement of one of the HO groups by Cl, and the removal of the H of the other as H_2O, this atom of H being then replaced by Cl; but this would require the calcium hydrate to absorb nearly an equal weight of chlorine, whereas the amount never exceeds half this quantity.

According to another view, the chloride of lime is a mixture of calcium hypochlorite, $Ca(ClO)_2$, with calcium oxychloride, $Ca_3O_2Cl_2$, produced by the reaction $4Ca(HO)_2 + Cl_4 = Ca(ClO)_2 + Ca_3O_2Cl_2 + 4H_2O$, which would require the absorption of nearly half its weight of chlorine by the calcium hydrate. A more recent theory regards the chloride of lime as containing calcium chloride, together with the compound $CaHClO_2$, resulting from the substitution of Cl for H in CaH_2O_2; but since calcium chloride absorbs water and becomes wet on exposure to air, whilst good chloride of lime remains dry, it is difficult to admit the correctness of this view. The analyses which support this theory would also agree equally well with the formula $Ca_3(OH)_2(OCl)_2Cl_2$, which would explain the tendency of chloride of lime to yield, among the products of its decomposition, calcium chloride, $CaCl_2$, calcium hypochlorite, $Ca(OCl)_2$ and calcium hydrate, $Ca(OH)_2$.

Practically, the constitution of chloride of lime itself is of less importance than that of the solution obtained by treating it with water, which is generally admitted to contain calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride, $CaCl_2$, with some calcium hydrate, $Ca(HO)_2$, of which a large quantity is left in the undissolved residue.

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* Calcium hypochlorite has been obtained in crystals of the formula $Ca(ClO)_2.4H_2O$ by evaporating solution of chloride of lime *in vacuo* over sulphuric acid and potash. The hypochlorites of lanthanium and didymium have also been crystallised.

Taking each of the three views above mentioned, the action of water upon chloride of lime would be represented by one of the following equations:

(1) $2CaCl(ClO) = CaCl_2 + Ca(ClO)_2$;
(2) $Ca(ClO)_2 + Ca_3O_2Cl_2 + 2H_2O = Ca(ClO)_2 + CaCl_2 + 2Ca(HO)_2$;
(3) $2CaHClO_2 + CaCl_2 = Ca(ClO)_2 + CaCl_2 + Ca(HO)_2$.

If the solution of chloride of lime be added to blue litmus, it will be found to exert little bleaching action; but on adding a little acid (sulphuric, for example), the blue colour will be discharged, the acid setting free the chlorine, which acts upon the colouring matter—

$$\underset{\text{Solution of }\textit{chloride of lime.}}{Ca(ClO)_2 + CaCl_2} + 2H_2SO_4 = 2CaSO_4 + 2H_2O + Cl_4.$$

Even carbonic acid will develop the bleaching property of chloride of lime, so that the above mixture may be decolorised by breathing into it through a glass tube.

When chloride of lime is used for bleaching on the large scale, the stuff to be bleached is first thoroughly cleansed from any grease or *weaver's dressing*, by boiling it in lime-water and in a weak solution of soda, and is then immersed in a weak solution of the chloride of lime. This, by itself, however, exerts very little action upon the natural colouring matter of the fibre, and the stuff is therefore next immersed in very dilute sulphuric acid, when the colouring matter is so far altered as to become soluble in the alkaline solution in which it is next immersed, and a repetition of these processes, followed up by a thorough rinsing, generally perfects the bleaching.

The property possessed by acids of liberating chlorine from the chloride of lime is applied, in calico-printing, to the production of white patterns upon a red ground. The stuff having been dyed with Turkey red, the pattern is imprinted upon it with a *discharge* consisting of an acid (tartaric, phosphoric, or arsenic) thickened with gum. On passing the fabric through a bath of weak chloride of lime, the colour is discharged only at those parts to which the acid has been applied, and where, consequently, chlorine is liberated.

Chloride of lime is one of the most convenient forms in which to apply chlorine for the purposes of fumigating and disinfecting. If a cloth saturated with the solution be suspended in the air, the carbonic acid gas in the latter causes a slow evolution of hypochlorous acid, which is even a more powerful disinfectant than chlorine itself. In extreme cases, where a rapid evolution of chlorine is required, the bleaching powder is placed in a plate, and diluted sulphuric acid is poured over it, or the powder may be mixed with half its weight of powdered alum in a plate, when a pretty rapid and regular escape of chlorine will ensue.

When chloride of lime is distilled with a small quantity of diluted sulphuric acid, a solution of hypochlorous acid is obtained; but if an excess of acid be used, free chlorine is the result.

Bleaching powder is liable to decomposition when kept, evolving oxygen, and becoming converted into calcium chloride, which attracts moisture greedily, and renders the bleaching powder deliquescent. It has been known to shatter the glass bottle in which it was preserved, in consequence of the accumulation of oxygen;* $CaOCl_2 = CaCl_2 + O$.

When a solution of a salt of manganese or cobalt is added to solution of chloride of lime, a black precipitate of MnO_2 or Co_2O_3 is obtained. If this precipitate be boiled with an excess of solution of chloride of lime, it causes a rapid disengagement of oxygen, in some manner that has not yet been clearly explained. Large quantities of oxygen are easily obtained by adding a few drops of solution of cobalt nitrate to solution of chloride of lime, and applying a gentle heat.

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* When rapidly made and hastily packed, it has been known to become so hot as to set fire to the casks.

Old chloride of lime always contains calcium chlorate; $6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2$.

Sodium hypochlorite, which is very useful for removing ink, is prepared in solution by decomposing solution of chloride of lime with solution of sodium carbonate, and separating the calcium carbonate by filtration. The solution is generally called "chloride of soda" (*liquor sodæ chloratæ*).

113. *Chloric acid* ($HClO_3$).—This acid is appropriately studied here, since its salts are usually obtained by the decomposition of the hypochlorites. The only chlorate which possesses any great practical importance is potassium chlorate ($KClO_3$), which is largely employed as a source of oxygen, as an ingredient of several explosive compositions, and in the manufacture of lucifer matches.

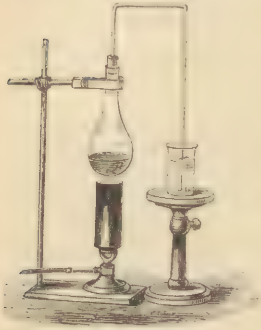

Fig. 174.

Potassium chlorate, or *chlorate of potash.*—The simplest method of obtaining this salt consists in passing an excess of chlorine rapidly into a strong solution of potash (fig. 174), when the liquid becomes hot enough to decompose the hypochlorite first formed into potassium chloride, which remains in solution, and potassium chlorate, which is deposited in tabular crystals, the ultimate result being expressed by the equation—

$$6KHO + Cl_6 = KClO_3 + 5KCl + 3H_2O.$$

If potassium carbonate or a weak solution of potash be employed, the liquid will require boiling after saturation with chlorine, in order to convert the hypochlorite into chlorate.

The following proportions will be found convenient for the preparation of potassium chlorate on the small scale as a laboratory experiment. 300 grains (or 20 grms.) of potassium carbonate are dissolved, in a beaker, with 2 measured ounces (or 60 c.c.) of water. 600 grains (or 40 grms.) of common salt are mixed with 450 grains (or 30 grms.) of binoxide of manganese, and very gently heated in a flask (fig. 174) with a mixture of 1½ ounce (measured) (or 40 c.c.) of strong sulphuric acid and 4 ounces (measured) (or 110 c.c.) of water, the evolved chlorine being passed through a rather wide bent tube into the solution of potassium carbonate.

At first no action will appear to take place, although the solution absorbs the chlorine; because the first portion of that gas converts the potassium carbonate into a mixture of potassium hypochlorite, potassium chloride, and hydropotassium carbonate, some crystals of which will probably be deposited; $2K_2CO_3 + Cl_2 + H_2O = KCl + KClO + 2KHCO_3$. On continuing to pass chlorine, these crystals will redissolve, and brisk effervescence will be caused by the expulsion of the carbonic acid gas: $2KHCO_3 + Cl_2 = KCl + KClO + H_2O + 2CO_2$. When this effervescence has ceased, and the chlorine is no longer absorbed by the liquid, the change is complete, the ultimate result being represented by the equation $K_2CO_3 + Cl_2 = KCl + KClO + CO_2$. The solution (which often has a pink colour, due to a little potassium ferrate) is now poured into a dish, boiled for two or three minutes, filtered, if necessary, from any impurities (silica, &c.) derived from the potassium carbonate, and set aside to crystallise. The ebullition has converted the potassium hypochlorite into chlorate and chloride of potassium; $3KClO = KClO_3 + 2KCl$.

The latter, being soluble in about three times its weight of cold water, is retained in the solution, whilst the chlorate, which would require about sixteen times its weight of cold water to hold it dissolved, is deposited in brilliant rhomboidal tables. These crystals may be collected on a filter, and purified from the adhering solution of potassium chloride by pressure between successive portions of filter-paper. If they be free from chloride, their solution in water will not be changed by silver nitrate, which would yield a milky precipitate of silver chloride if that impurity were present. Should this be the case, the crystals must be redissolved in a small quantity of boiling water, and recrystallised.

The above processes for preparing potassium chlorate are far from economical, since five-sixths of the potash are converted into chloride, being employed merely to furnish oxygen to convert the chlorine into chloric acid. In manufacturing the chlorate upon the large scale, a much cheaper material, lime, is used to furnish the oxygen, one molecule of potassium carbonate being mixed with six molecules of slaked lime and the damp mixture saturated with chlorine. On treating the mass with boiling water, a solution is obtained which contains potassium chlorate and calcium chloride: the latter, being very soluble, remains in the liquor, from which the chlorate crystallises on cooling. The ultimate result of the action of chlorine upon the mixture of potassium carbonate and lime is thus expressed—

$$K_2CO_3 + 6Ca(HO)_2 + Cl_{12} = 2KClO_3 + 5CaCl_2 + CaCO_3 + 6\,H_2O.$$

A still cheaper salt of potassium, the chloride, has recently been employed with great economy as a substitute for the carbonate. Lime is mixed with water, and saturated with chlorine gas in close leaden tanks; $2Ca(OH)_2$ (calcium hydrate) + Cl_4 = $Ca(OCl)_2$ (calcium hypochlorite) + $CaCl_2$ (calcium chloride) + $2H_2O$. The liquid is boiled down, when the calcium hypochlorite is decomposed into calcium chlorate and chloride; $3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2$. The calcium chlorate is now decomposed by boiling with potassium chloride, when it yields calcium chloride which remains in solution, and potassium chlorate which separates in crystals as the solution cools—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

Chloric acid ($HClO_3$) may be procured by decomposing a solution of potassium chlorate with hydrofluosilicic acid, when the potassium is deposited as an insoluble silico-fluoride, and chloric acid is found in the solution;* $2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6$.

On evaporating the solution at a temperature not exceeding 100° F. (38° C.), the chloric acid is obtained as a yellow liquid, with a peculiar pungent smell, having the composition $HClO_3.7Aq$.

In its chemical characters, chloric acid bears a very strong resemblance to nitric acid, but is far more easily decomposed. It cannot even be kept unchanged for any length of time, and at temperatures above 104° F. (40° C.) it is decomposed into perchloric acid, chlorine, and oxygen; $4HClO_3 = 2HClO_4 + H_2O + Cl_2 + O_3$.

Chloric acid is one of the most powerful oxidising agents: a drop of it will set fire to paper, and it oxidises phosphorus (even the amorphous variety) with explosive violence.

114. *Chlorates.*—Chloric acid, like nitric, is monobasic, containing only one atom of hydrogen replaceable by a metal. The chlorates resemble the nitrates in their oxidising power, but generally act at

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* 440 grain measures of hydrofluosilicic acid of sp. gr. 1078 will decompose 100 grains of the chlorate.

lower temperatures, in consequence of the greater facility with which the chlorates part with their oxygen.

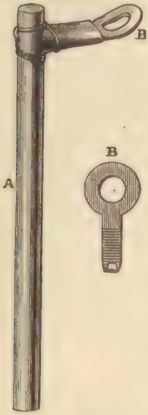

Fig. 175.

A grain or two of potassium chlorate, rubbed in a mortar with a little sulphur, for example, detonates violently, evolving a powerful odour of chloride of sulphur. Potassium chlorate and sulphur were used in some of the first percussion caps, but being found to corrode the nipple of the gun, they gave place to the *anticorrosive caps* containing mercuric fulminate.

If a little powdered chlorate be mixed on a card with some black antimony sulphide, and wrapped up in paper, the mixture will detonate when struck with a hammer.

A mixture of this description is employed in the *friction tubes* used for firing cannon. These are small tubes (A, fig. 175) of sheet copper (for military) or of quill (for naval use), filled with gunpowder: in the upper part of the tube a small copper rasp (B) is tightly fixed across it, and on each side of the rasp a pellet is placed containing 12 parts of potassium chlorate, 12 of antimony sulphide, and 1 of sulphur, these ingredients being worked up into a paste with a solution of an ounce of shellac in a pint of spirit of wine. The friction tube is fixed in the vent of the gun, and the copper rasp quickly withdrawn by a cord in the hands of the gunner, when the detonating pellets explode and fire the powder. The earliest lucifer matches were tipped with a mixture of potassium chlorate, antimony sulphide, and starch, and were kindled by drawing them briskly through a doubled piece of sand-paper.

A mixture of potassium chlorate and lead ferrocyanide is used in toy detonating crackers.

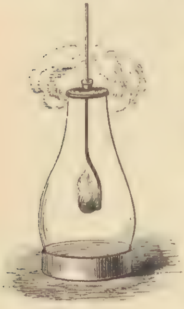
Fig. 176.

At high temperatures the chlorates act violently upon combustible bodies. A little potassium chlorate sprinkled upon red-hot coals causes a very violent deflagration. If a little of the chlorate be melted in a deflagrating spoon, and plunged into a bottle or flask containing coal gas (fig. 176), the salt burns with great brilliancy, its oxygen combining with the carbon and hydrogen in the gas, which becomes in this case the *supporter of combustion.* The flask may be conveniently filled with coal gas by inverting it, and passing a flexible tube from the gas pipe up into it.

Potassium chlorate is much used in the manufacture of fireworks, especially as an ingredient of coloured fire compositions, which generally consist of potassium chlorate mixed with sulphur, and with some metallic compound, to produce the desired colour in the flame. They are not generally made of the best quality on the small scale, from want of attention to the very finely powdered state of the ingredients, the absence of all moisture, and the most intimate mixture.

If these precautions be attended to, the following prescriptions will give very good coloured fires :—

Red fire.—40 grains of strontium nitrate, thoroughly dried over a lamp, are mixed with 10 grains of potassium chlorate, and reduced to the finest possible powder. *In another mortar* 13 grains of sulphur are mixed with 4 grains of black sulphide of antimony (crude antimony). The two powders are then placed upon a sheet of paper, and very intimately mixed with a bone knife, avoiding any great pressure. A little heap of the mixture touched with a red-hot iron ought to burn with a uniform red flame, the colour being due to the strontium.*

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* The red fire made by pyrotechnists commonly contains charcoal 1 part shellac 4 parts, sulphur 8 parts, potassium chlorate 12 parts, strontium nitrate 40 parts.

Blue fire.—15 grains of potassium chlorate are mixed with 10 grains of potassium nitrate and 30 grains of oxide of copper, in a mortar. The finely powdered mixture is transferred to a sheet of paper, and mixed, by a bone knife, with 15 grains of sulphur. The colour of the fire is given chiefly by the copper.

Green fire.—10 grains of barium chlorate are mixed with 10 grains of barium nitrate in a mortar, and afterwards on paper with 12 grains of sulphur. The barium is the cause of the bright green colour of the flame.

These compositions are rather dangerous to keep, since they are liable to spontaneous combustion.

White gunpowder is a mixture of two parts of potassium chlorate with one part of dried yellow prussiate of potash, and one part of sugar, which explodes very easily under friction or percussion.

The decomposition of potassium chlorate by heat into oxygen and potassium chloride is attended with evolution of heat, unlike most cases of chemical decomposition, in which heat is generally absorbed. If the chlorate be heated to the point at which it begins to decompose, and a little ferric oxide be thrown into it, enough heat will be evolved to bring the mass to a red heat, although the ferric oxide is not oxidised. Experiment has shown that one part of chlorate evolves, during decomposition, nearly 39 units of heat, or enough heat to raise 39 parts of water through 1° C. This anomalous evolution of heat must of course contribute to increase the energy of explosive mixtures containing the chlorate, and may be accounted for on the supposition that the heat evolved by the combination of the potassium with the chlorine to form potassium chloride exceeds that which is absorbed in effecting the chemical decomposition of the chlorate.

115. *Perchloric acid* ($HClO_4$) is obtained by evaporating down, at a boiling heat, the solution of chloric acid obtained by decomposing potassium chlorate with hydrofluosilicic acid (see page 163), when the chloric acid is decomposed into perchloric acid, chlorine, and oxygen; $4HClO_3 = 2HClO_4 + H_2O + Cl_2 + O_3$.

When the greater part of the water has been boiled off, the liquid may be introduced into a retort and distilled. After the remainder of the water has passed over, it is followed by a heavy oily liquid, which is $HClO_4.2H_2O$. If this be mixed with four times its volume of strong sulphuric acid and again distilled, the pure perchloric acid ($HClO_4$) first passes over as a yellow watery liquid. If the distillation be continued, the oily $HClO_4.2H_2O$ distils over, and if this be mixed with the former and cooled, it yields silky crystals containing $HClO_4.H_2O$, which are decomposed at 230° F. (110° C.) into $HClO_4$, which may be distilled off, and $HClO_4.2H_2O$, which is left in the retort—

$$2(HClO_4.H_2O) = HClO_4 + HClO_4.2H_2O.$$

The pure perchloric acid is a colourless, very heavy liquid (sp. gr. 1.782), which soon becomes yellow from decomposition. It cannot be kept for any length of time. When heated, it undergoes decomposition, often with explosion. In its oxidising properties it is more powerful than chloric acid. It burns the skin in a very serious manner, and sets fire to paper, charcoal, &c., with explosive violence. This want of stability, however, belongs only to the pure acid. If water be added to it, heat is evolved, and a diluted acid of far greater permanence is obtained. Diluted perchloric acid does not even bleach, but reddens litmus in the ordinary way.

Perchloric acid is monobasic. The *perchlorates* are decomposed by heat, evolving hydrogen, and leaving chlorides; thus—$KClO_4 = KCl + O_4$.

The potassium perchlorate is always formed in the first stage of the decomposition of potassium chlorate by heat;

$$2KClO_3 = KClO_4 + KCl + O_2.$$

If a few crystals of potassium chlorate be heated in a test-tube, they first melt to a perfectly clear liquid, which soon evolves bubbles of oxygen. After a time the liquid becomes pasty, and if the contents of the tube, after cooling, be dissolved by boiling with water, the latter will deposit, as it cools, crystals of potassium perchlorate. These are readily distinguished from chlorate by their not yielding a yellow gas (ClO_2) when treated with strong sulphuric acid. The perchlorate is remarkable as one of the least soluble of the potassium salts, requiring 150 times its weight of cold water to dissolve it. Neither perchloric acid nor any of its salts is applied to any useful purpose.

116. *Chloric peroxide* or *peroxide of chlorine* (ClO_2) is dangerous to prepare and examine on account of its great instability and violently explosive character. It is obtained by the action of strong sulphuric acid upon potassium chlorate—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + 2ClO_2 + H_2O.$$

It is a bright yellow gas, with a chlorous and somewhat aromatic smell, and sp. gr. 2.32; condensable at $-4°$ F. to a red, very explosive liquid. The gas is gradually decomposed into its elements by exposure to light, and a temperature of 140° F. (60° C.) causes it to decompose with violent explosion into a mixture of chlorine and oxygen, the volume of which is one-third greater than that of the compound.

On a small scale, chloric peroxide may be prepared with safety by pouring a little strong sulphuric acid upon one or two crystals of potassium chlorate, in a test-tube supported in a holder. The crystals at once acquire a red colour, which gradually diffuses itself through the liquid, and the bright yellow gas collects in the tube. If heat be applied, the gas will explode, and the colour and odour of chloric peroxide will be exchanged for those of chlorine. If the chlorate employed in this experiment contains potassium chloride, explosion often takes place in the cold, since the hydrochloric acid evolved by the action of the acid upon that salt decomposes a part of the chloric peroxide, and thus provokes the decomposition of the remainder.

Chloric peroxide is easily absorbed by water, and the solution has powerful bleaching properties. Combustible bodies, such as sulphur and phosphorus, decompose the gas, as might be expected, with great violence. This powerful oxidising action of chloric peroxide upon combustible substances appears to be the cause of the property possessed by mixtures of such substances with potassium chlorate, to inflame when touched with strong sulphuric acid.

If a few crystals of potassium chlorate be thrown into a glass of water (fig. 177), one or two small fragments of phosphorus dropped upon them, and some strong sulphuric acid poured down a funnel tube to the bottom of the glass, the chloric peroxide will inflame the phosphorus with bright flashes of light and slight detonations.

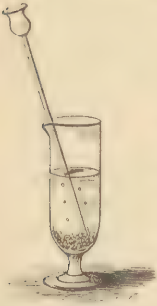
Fig. 177.

Powdered sugar mixed with potassium chlorate on paper, will burn brilliantly when touched with a glass rod dipped in strong sulphuric acid. Matches may be prepared, which inflame when moistened with sulphuric acid, by dipping the ends of splinters of wood in melted sulphur, and, when cool, tipping them with a mixture of 5 grains of sugar and 15 grains of potassium chlorate made into a paste with 4 drops of water. When dry, they may be fired by dipping them into a bottle containing asbestos moistened with strong sulphuric acid. These matches, under the names of Eupyrion and Vesta matches, were used before the introduction of phosphorus into general use. The Promethean light was an ornamental scented paper spill, one end of which contained a small glass bulb of sulphuric acid surrounded with a mixture of chlorate and sugar, which inflamed when the end of the spill was struck or squeezed, so as to break the bulb containing the sulphuric acid. The paper was waxed in order to make it inflame more easily. Percussion fuzes, &c., have been often constructed upon a similar principle.

Chloric peroxide used to be called hypochloric acid; but, like nitric peroxide, it appears to have no claim to be considered a true acid, since in contact with the alkalies, it yields mixtures of chlorites and chlorates; thus—$2ClO_2 + 2KHO = KClO_2 + KClO_3 + H_2O$.

117. *Euchlorine*, the deep yellow, dangerously explosive gas evolved by the action of strong hydrochloric acid upon potassium chlorate, appears to be a mixture of chloric peroxide with free chlorine. It is resolved by explosion into 2 vols. Cl and 1 vol. O. Mercurous chloride absorbs Cl from it, leaving ClO_2. Hence its production may be explained by the equation, $4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + Cl_3$.

The gas known as *chlorous anhydride* has been proved to be a mixture of ClO_2 and Cl.

CHLORIDES OF CARBON.

118. It has already been seen that chlorine has no direct attraction for carbon, the two elements not being known to enter into direct combination; but several chlorides of carbon may be obtained by the action of chlorine upon other compounds of carbon. Thus, if Dutch liquid ($C_2H_4Cl_2$), produced by the combination of olefiant gas with chlorine (p. 96), be acted upon with an excess of chlorine in sunlight, the whole of its hydrogen is removed in the form of hydrochloric acid, and an equivalent amount of chlorine is substituted for it, yielding the *trichloride*, formerly called *sesquichloride of carbon* (C_2Cl_6); $C_2H_4Cl_2 + Cl_8 = C_2Cl_6 + 4HCl$.

Carbon trichloride is a white crystalline solid, with an aromatic odour, rather like that of camphor. It fuses at 160° C., and boils at 182° C., subliming unchanged. It is not dissolved by water, but is soluble in alcohol and ether.

When the vapour of carbon trichloride is passed through a tube containing fragments of glass heated to redness, it is decomposed into chlorine and a colourless liquid, which is the dichloride, formerly called *protochloride of carbon* (C_2Cl_4). It has an aromatic odour, and boils at 120° C.: is heavier than water (sp. gr. 1.5), which does not dissolve it, and is soluble in alcohol and ether.

By passing the vapour of this carbon dichloride through tubes heated to bright redness, it is decomposed into chlorine and monochloride, formerly called *subchloride of carbon* (C_2Cl_2), which forms silky crystals almost free from odour, insoluble in water, but soluble in ether, and capable of being sublimed unchanged at a high temperaure. It burns in air with a red smoky flame.

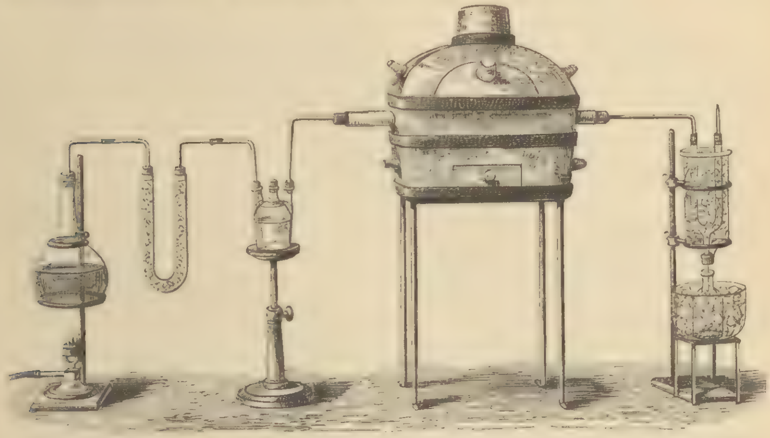

Fig. 178.—Preparation of carbon tetrachloride.

Carbon tetrachloride (CCl_4) has been mentioned (p. 152) as the final result of the action of chlorine upon marsh gas (CH_4) and upon chloroform ($CHCl_3$). It is easily obtained in large quantity, by passing chlorine (dried by passing through a tube containing pumice wetted with strong sulphuric acid) (fig. 178) through a bottle containing carbon disulphide, and afterwards through a porcelain tube, filled with fragments of broken porcelain, maintained at a red heat by a charcoal or gas furnace, and condensing the products in a bottle surrounded by ice. A mixture of carbon tetrachloride and sulphur dichloride is thus obtained; $CS_2 + Cl_6 = CCl_4 + S_2Cl_2$. By shaking this mixture with potash, the sulphur dichloride is decomposed and dissolved, whilst the carbon tetrachloride separates and falls to the bottom. The upper layer having been poured off, the tetrachloride may be purified by distillation.

Another method of preparing CCl_4 consists in distilling carbon disulphide with antimonic chloride in a stream of chlorine.

Carbon tetrachloride is a colourless liquid, much heavier than water (sp. gr. 1.6), having a peculiar odour, and boiling at 172° F. (78° C.). It may be solidified at $-9°$ F. The tetrachloride is insoluble in water, but dissolves in alcohol and ether.

By the action of chlorine on naphthalene ($C_{10}H_8$), Laurent obtained, as the ultimate result, a crystalline chloride of carbon containing $C_{10}Cl_8$, to which he gave the name *chlonaphthalise*.

It will be noticed that each of the compounds of chlorine with carbon, except the trichloride, has its parallel in the compounds of hydrogen with carbon;* thus—

Acetylene	C_2H_2	corresponds to the	monochloride	C_2Cl_2
Olefiant gas	C_2H_4	,,	dichloride	C_2Cl_4
Marsh gas	CH_4	,,	tetrachloride	CCl_4

The history of carbon trichloride affords an instructive instance of the influence of the molecular weight of a compound upon its properties. By passing the vapour of carbon tetrachloride through a tube heated to dull redness, a liquid is obtained which is found by analysis to contain precisely the same proportions of carbon and chlorine as the solid trichloride above described, but the specific gravity of its vapour ($H = 1$) is only 59.25, which is half that of the vapour of solid carbon trichloride, showing that in the liquid compound the same proportions of carbon vapour and chlorine are condensed into a volume twice as large as in the solid trichloride, and it must be represented by the formula CCl_3.

119. *Oxychloride of carbon, carbonyle chloride*, or *phosgene gas*, $COCl_2$, is produced by the direct combination of equal volumes of carbonic oxide and chlorine gases under the influence of sunlight (whence its last name), when the mixture condenses to half its volume of a colourless gas, condensable by cold, having a very peculiar pungent smell, and fuming strongly when exposed to moist air, decomposing the moisture and producing hydrochloric acid; $CO.Cl_2 + H_2O = CO_2 + 2HCl$. It is decomposed by alkalies, producing chlorides and carbonates.

$COCl_2$ may also be prepared by passing a mixture of equal volumes of CO and Cl through a long tube filled with granulated animal charcoal, which favours the combination of the gases; or by passing dried carbonic oxide through antimony pentachloride; $SbCl_5 + CO = COCl_2 + SbCl_3$.

Phosgene gas has also been obtained by heating carbon tetrachloride with phosphoric anhydride, in a sealed tube; $3CCl_4 + P_2O_5 = 2POCl_3 + 3COCl_2$; and by heating chloroform with sulphuric acid and potassium dichromate.

120. *Silicon tetrachloride*, unlike the chlorides of carbon, may be formed by the direct union of silicon with chlorine at a high temperature; but it is best prepared by passing dry chlorine over a mixture of silica and charcoal, heated to redness in a porcelain tube connected with a receiver kept cool by a freezing mixture. Neither carbon nor chlorine separately will act upon the silica, but when they are employed together,

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[*] When vapour of carbon dichloride is mixed with hydrogen, and passed through a red-hot tube, olefiant gas and hydrochloric acid are produced. The tetrachloride, under similar circumstances, yields marsh gas.

the carbon removes the oxygen and the chlorine combines with the silicon; $SiO_2 + C_2 + Cl_4 = SiCl_4 + 2CO$.

The tetrachloride is a colourless heavy liquid (sp. gr. 1.52), which is volatile (boiling point, 59° C.), and fumes when exposed to air, the moisture of which decomposes it, yielding hydrochloric acid and silica; $SiCl_4 + 2H_2O = SiO_2 + 4HCl$. Although it has received no practical application on a large scale, it is valuable to the chemist as a convenient source of compounds of silicon, which could not easily be procured from the very unchangeable silica.

Si_2Cl_6 is formed when $SiCl_4$ is passed over silicon at a very high temperature. Its vapour is said to be stable at temperatures below 350° C. and above 1000° C., but it cannot exist between those limits, being decomposed into silicon and $SiCl_4$.

By passing hydrochloric acid over silicon heated to redness, a very remarkable liquid is obtained, which is much more volatile than the chloride of silicon (boiling point, 42° C.), and, unlike most chlorine compounds, is inflammable, burning with a greenish flame, and producing silica and hydrochloric acid. This liquid is *silico-chloroform*, $SiHCl_3$, produced according to the equation, $Si + 3HCl = SiHCl_3 + H_2$. The corresponding bromine and iodine compounds are known. It fumes strongly in air, and is decomposed by water, yielding hydrochloric acid, and the substance termed leucone.

The *boron trichloride* (BCl_3) is similar in its general character to the silicon tetrachloride, and is prepared by a similar process, but it is a gas instead of a liquid at ordinary temperatures.

121. *Chloride of nitrogen* is the name usually given to the very explosive compound before referred to as being produced by the action of chlorine on sal ammoniac. Its composition is somewhat uncertain, its explosive character rendering its exact analysis very difficult. Some chemists regard it as NCl_3, that is, ammonia in which all the hydrogen has been displaced by chlorine, whilst others believe it to contain hydrogen, regarding it as derived from two molecules of ammonia ($NH_3.NH_3$), by the substitution of five atoms of chlorine for five of hydrogen ($NCl_3.NHCl_2$).

It is a yellow, heavy, oily liquid (sp. gr. 1.65), which volatilises easily, yielding a vapour of very characteristic odour, which affects the eyes. When heated to about 200° F. it explodes with great violence, emitting a loud report and a flash of light.* Its instability is, of course, attributable to the feeble attraction which holds its elements together; and the violence of the explosion, to the sudden expansion of a small volume of the liquid into a large volume of nitrogen, chlorine, and perhaps hydrochloric acid. As might be expected, its explosion is at once brought about by contact with substances which have an attraction for chlorine, such as phosphorus and arsenic; the oils and fats cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently; whilst acids, having no action upon the chlorine, are not so liable to explode it. At 160° F. this substance has actually been distilled without explosion.

Although practically unimportant, the violent explosive properties of this substance render it so interesting that it may be well to give some directions for its safe preparation, which may be effected by the action of solution of hypochlorous acid upon ammonium chloride.

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* It is said to absorb 38,478 gramme-degrees of heat per equivalent, in the process of formation, and would therefore disengage that amount of heat in the act of decomposition.

Fifty grains of red oxide of mercury are very finely powdered, and thrown into a pint bottle of chlorine together with ½ oz. (measured) of water. The stopper is replaced, and the bottle well shaken, loosening the stopper occasionally, as long as the chlorine is absorbed. The solution of hypochlorous acid thus produced is filtered from the residual mercuric oxychloride, and poured into a clean *thumb-glass* (fig. 179). A lump of sal ammoniac weighing 20 grains is then dropped into the solution, and the glass is placed under a stout wooden box. After the lapse of twenty minutes, the chloride of nitrogen may be exploded by inserting, through a hole in the box, a stick dipped in turpentine, fixed at right angles to a longer stick. The glass will be shattered into very small fragments.

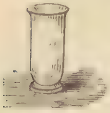
Fig. 179.

122. *Aqua regia.*—This name has been bestowed upon the mixture of 1 measure of nitric, and 3 measures of hydrochloric acid (*nitro-muriatic acid*), which is employed for dissolving gold, platinum, and other metals which are not soluble in the separate acids. If a little gold leaf be placed in hydrochloric and nitric acids contained in separate glasses, the metal will remain unaffected even on warming the acids; but if the contents of the glasses be mixed, the gold will be immediately dissolved by the chlorine, which is liberated in the action of the acids upon each other; $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$.

The *nitrosyle chloride* (NOCl) is a red gas, condensable in a freezing mixture to a dark red liquid, which boils at 18° F. It has a very peculiar odour, and is decomposed by contact with water. Nitrosyle chloride is also produced by mixing 2 volumes of nitric oxide with 1 volume of chlorine; it condenses to a red liquid at 0° F. When nitrosyle chloride is passed into oil of vitriol cooled to 32° F., crystals of the acid nitrosyle sulphate are deposited; $NOCl + H_2SO_4 = HCl + NOHSO_4$.

Nitrosyle sulphate is also obtained by passing SO_2 into nitric acid, or N_2O_3 into sulphuric acid, or by burning a mixture of 1 part of sulphur and 3 parts of nitre in moist air. When heated with KNO_3, nitrosyle sulphate yields *nitrosyle nitrate*, $NO.NO_3$, which is identical with N_2O_4.

BROMINE.

Br = 80 parts by weight.

123. It generally happens that elements between which any strong family likeness exists are found associated in nature. This remark particularly applies to the three elements—chlorine, bromine, and iodine—all of which are found in sea water, though the first predominates to such an extent that the others for a long time escaped notice. Bromine was brought to light in the year 1826 by Balard in the examination of *bittern*, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallise by evaporating sea water, which contains bromine in the forms of bromide of magnesium and bromide of sodium.* It is also extracted from the waters of certain mineral springs, as those of Kreuznach and Kissingen, which contain much larger quantities of bromine, combined with potassium, sodium, or magnesium. During the last few years much bromine has been obtained from the mother-liquors of the salt-works at Stassfurt, and from saline springs in the United States.

In extracting the bromine from these waters, advantage is taken of the circumstance that chlorine is capable of displacing bromine from its combinations with the metals. After most of the other salts, such as sodium chloride, sodium sulphate, and magnesium sulphate, which are less soluble than the bromides, have been separated from the water by evaporation and crystallisation, the remaining liquid is subjected to the action of chlorine gas, when it acquires an orange colour, due to the liberation of the bromine; $KBr + Cl = KCl + Br$. The bromine thus set free exists now diffused through a large volume of water, which cannot be separated from it in the usual way, by evaporation, because bromine is itself very volatile. An ingenious expedient is therefore resorted to, of shaking the orange liquid briskly with ether, which has a greater solvent power for bromine than is possessed by water, and therefore abstracts it from the aqueous solution: since ether does not mix to any great extent with water, it now rises to the surface of the liquid, forming a layer of a beautiful orange colour, due to the bromine which it holds in solution. This orange layer is carefully separated, and shaken with solution of potash, which immediately destroys the colour by removing the bromine, leaving the ether to rise to the surface in a pure state, and fit to be employed for abstracting the bromine from a fresh portion of the water. The action of the bromine upon potash is precisely similar to that of chlorine—

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* 4·9 grs. per gallon of magnesium bromide have been found in the water of the Irish Channel.

$$6KHO + Br_6 = 5KBr + KBrO_3 + 3H_2O.$$

After the solution of potash has been several times shaken with the ethereal solution of bromine, and has become highly charged with this element, it is evaporated so as to expel the water, leaving a solid residue containing the potassium bromide and bromate. This saline mass is strongly heated to decompose the bromate, and convert it into bromide; $KBrO_3 = KBr + O_3$. From this salt the bromine is extracted by distilling it with manganese dioxide and sulphuric acid, when the bromine is liberated and condensed in a receiver kept cold by iced water—

$$2KBr + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

The extraction of bromine is very often combined with that of iodine as described at page 174.

The aspect of bromine is totally different from that of any other element, for it distils over in the liquid condition, and preserves that form at ordinary temperatures, being the only liquid non-metallic element. Its dark red-brown colour, and the peculiar orange colour of the vapour which it exhales continually, are also characteristic; but, above all, its extraordinary and disagreeable odour, from which it derives its name (*βρῶμος, a stench*), leaves no doubt of its identity. The odour has some slight resemblance to that of chlorine, but is far more intolerable, often giving rise to great pain, and sometimes even to bleeding at the nose.

Liquid bromine is thrice as heavy as water (sp. gr. 2.96), and boils at 58°.7 C., yielding a vapour $5\frac{1}{2}$ times as heavy as air (sp. gr. 5.54). It may be frozen at $-7°$ C. to a brown crystalline solid. It requires 33 times its weight of cold water to dissolve it, and is capable of forming a crystalline aquate ($Br.5H_2O$) corresponding to chlorine aquate.

In its bleaching power, its aptitude for direct combination, and its other chemical characters, it very closely resembles chlorine, so closely, indeed, that it is difficult to distinguish, in many cases, between the compounds of chlorine and bromine with other substances, unless the elements themselves be isolated. A necessary consequence of so great a similarity is, that very little use has been made of bromine, since the far more abundant chlorine fulfils nearly all the purposes to which bromine might otherwise be applied. In the daguerreotype and photographic arts, however, some special applications of bromine have been discovered, and for some chemical operations, such as the determination of the illuminating hydrocarbons in coal gas, bromine is sometimes preferred to chlorine. It has also been used in America as a disinfectant. The bromides of potassium and ammonium are frequently employed in medicine. Bromide of cadmium is used in photography. Commercial bromine sometimes contains bromoform and cyanogen bromide. In the composition of their compounds chlorine and bromine exhibit great analogy, but no compound of bromine with oxygen has been obtained.

Hypobromous acid ($HBrO$) has been obtained in solution by shaking mercuric oxide with water and bromine. The solution is very unstable, decomposing, especially when heated, with liberation of bromine and formation of bromic acid. The action of bromine upon diluted solutions of the alkalies, and upon the alkaline earths, produces bleaching liquids similar to those formed by chlorine, and apparently containing the hypobromites of the metals.

Bromic acid ($HBrO_3$) can be prepared in a similar manner to chloric acid, to which it has a great general resemblance, the bromates being also similar to the chlorates.

Perbromic acid ($HBrO_4$) is obtained by the action of perchloric acid upon bromine.

124. *Hydrobromic acid* (HBr = 81 parts by weight = 2 volumes).—The inferiority of bromine to chlorine in chemical energy is well exemplified in its relations to hydrogen; for the vapour of bromine mixed with hydrogen will not combine under the action of flame or of the electric spark, like the mixture of chlorine and hydrogen. Direct combination may, however, be slowly induced by contact with heated platinum.

When it is attempted to prepare this acid by distilling bromide of sodium or potassium with sulphuric acid (as in the preparation of hydrochloric acid) the inferior stability of hydrobromic acid is shown by the decomposition of a part of it, the hydrogen being oxidised by the sulphuric acid, and the bromine set free; $2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$.

If a strong solution of phosphoric acid be employed instead of the sulphuric, pure hydrobromic acid may be obtained.

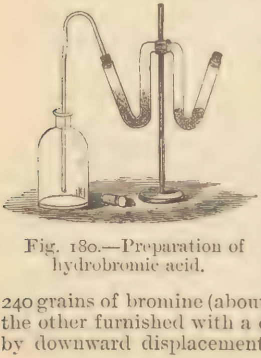

Fig. 180.—Preparation of hydrobromic acid.

But the most instructive method of obtaining hydrobromic acid consists in attacking water with bromine and phosphorus simultaneously, when the phosphorus takes the oxygen of the water, forming phosphoric acid, and the bromine combines with the hydrogen to form hydrobromic acid—

$$3H_2O + Br_5 + P = \underset{\text{Phosphoric acid.}}{HPO_3} + 5HBr.$$

The experiment may be made in a W-formed tube (fig. 180), one bend of which contains 40 grains of phosphorus in fragments intermingled with glass moistened with water, whilst the other bend contains 240 grains of bromine (about 1 drachm). This limb of the tube is corked, and the other furnished with a delivery tube, so that the gas may be collected either by downward displacement or over mercury. The bromine is slightly heated, when it distils over to the moist phosphorus, and hydrobromic acid is evolved. A moderate heat should afterwards be applied to the moist glass, to expel part of the hydrobromic acid from the water.

Hydrobromic acid is very similar to hydrochloric acid; it liquefies at −92° F. Like that gas, it is very soluble in water, and the solution acts upon metals and their oxides in the same manner as hydrochloric acid. Chlorine removes the hydrogen from hydrobromic acid, liberating bromine, which it converts into *chloride of bromine* if employed in excess.

Bromide of nitrogen has been obtained by the action of bromide of potassium upon chloride of nitrogen, which it resembles in general character and explosive properties.

Carbon tetrabromide, CBr_4, is obtained by heating CCl_4 with aluminium bromide in a sealed tube to 100° C. *Silicon tetrabromide*, $SiBr_4$, is also known. *Silicon tribromochloride*, $SiBr_3Cl$, has been obtained as a liquid boiling at 140° C.

Chloride of bromine, $BrCl$, is a very volatile red-brown liquid of pungent odour. It is decomposed above 10° C. That chlorine should unite directly with bromine, which it so much resembles in chemical character, illustrates its great tendency to direct chemical combination.

IODINE.

$I = 127$ parts by weight.

125. Iodine is contained in sea water in even smaller quantity than bromine, and appears to be present as *calcium iodate*, $Ca(IO_3)_2$, of which 4 parts are contained in a million of sea water,* but the iodine appears to constitute a portion of the necessary food of certain varieties of seaweed, which extract it from the sea water, and concentrate it in their tissues. The ash remaining after sea-weed has been burnt was long used, under the name of *kelp*, in soap-making, because it contains a considerable quantity of sodium carbonate; and in the year 1811, Courtois, a soap-boiler of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance which possessed properties different from those of any form of matter with which he was acquainted. He transferred it to a French chemist, Clement, who satisfied himself that it was really a new substance; and Gay-Lussac and Davy having examined it still more closely, it took its rank among the non-metallic elementary substances, under the name of iodine (*ιοειδής, violet-coloured*), conferred upon it in allusion to the magnificent violet colour of its vapour.

This history of the discovery of iodine affords a very instructive example of the advantage of training persons engaged in manufactures to habits of accurate observation, and, if possible, of accurate chemical observation; for had Courtois passed over this new substance as accidental, or of no consequence, the community would have lost, at least for some time, the benefits derived from the discovery of iodine.

For some years the new element was only known as a chemical curiosity, but an unexpected demand for it at length arose on the part of the physician, for it had been found that the efficacy of the ashes of

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* The iodate may be detected in sea water by shaking with carbon disulphide and a little of the water in which phosphorus has been kept; the phosphorous acid reduces the iodate, liberating iodine, which dissolves in the CS_2 with a rose colour.

sponge, which had long been used in some particular maladies, was due to the small quantity of iodine which they contained, and it was of course thought desirable to place this remedy in the hands of the medical profession in a purer form than the ash of sponge, where it is associated with very large quantities of various saline substances. Much more recently, the demand for this element has greatly increased on account of its employment in photography, and large quantities of it are annually produced from kelp, the collection and burning of which affords occupation to the very poor inhabitants of some parts of the coasts of Ireland and Scotland, who would otherwise have been thrown out of work when soda began to be manufactured from common salt, and the demand for kelp as the source of that alkali had ceased. The sea-weed * is spread out to dry, and burnt in shallow pits at as low a temperature as possible; for the sodium iodide is converted into vapour and lost if the temperature be very high. The ash, which is left in a half-fused state, is broken into fragments and treated with hot water, which dissolves about half of it, leaving a residue consisting of calcium carbonate and sulphate, sand, &c. The whole of the sodium iodide is contained in the portion dissolved by the water, but is mixed with much larger quantities of sulphate, carbonate, hyposulphite, sulphide and bromide of sodium, together with sulphate and chloride of potassium. A portion of the water is expelled by evaporation, when the sulphate and carbonate of sodium and chloride of potassium, being far less soluble than the iodide of sodium, crystallise out. In order to decompose the hyposulphite and sulphide of sodium, the liquid is mixed with an eighth of its bulk of oil of vitriol, which decomposes these salts, evolving sulphurous and hydrosulphuric acid gases, with deposition of sulphur, and forming sodium sulphate, which is deposited in crystals. The liquor thus prepared is next mixed with manganese dioxide, and heated in an iron still lined with lead (fig. 181), when the iodine is evolved as a magnificent purple vapour, which condenses in the globular glass or stoneware receivers (*aludels*) in the form of dark grey scales with metallic lustre, and having considerable resemblance to black lead. The liberation of the iodine is explained by the following equation—
$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2$.

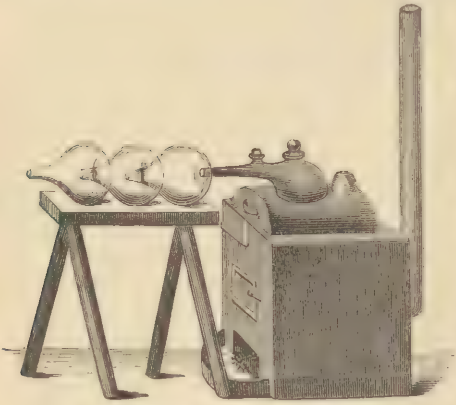

Fig. 181.—Extraction of iodine.

When no more iodine passes over, some more manganese dioxide is added, and the bromine then distils. The quantity of bromine obtained is about one-tenth that of the iodine. A ton of kelp yields about 10 lbs. of iodine.

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* The *Laminaria digitata*, or deep sea tangle, contains most iodine, amounting to 0.45 per cent. of the dried weed.

Several processes have been devised to render the extraction of the iodine from the concentrated solution of kelp easier and more economical. The most promising is very similar to that employed for separating bromine (p. 170). The iodine is liberated by chlorine, and extracted from the liquid by shaking it with benzene; by treating the benzene with solution of potash, the iodine is converted into a mixture of potassium iodide and iodate, from which the iodine may be precipitated by acidifying with hydrochloric acid—$6KHO + I_6 = 5KI + KIO_3 + 3H_2O$; $5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + I_6$. A far more economical process for the treatment of sea-weed consists in distilling it, when ammonia, acetic acid, naphtha, tar, and illuminating gas are obtained, whilst a porous charcoal remains in the retort, which is treated with water in order to extract the iodides and other soluble salts. This charcoal somewhat resembles animal charcoal in character, containing much phosphate and carbonate of calcium and magnesium; it is useful as a decolorising and deodorising agent. Iodine is now extracted from the deposits of nitrate of soda occurring in Chili, which contain sodium iodate ($NaIO_3$). It has also been found in France in some kinds of apatite.

The features of this element are extremely well marked: its metallic lustre and peculiar odour sufficiently distinguish it from all others, and the effect of heat upon it is very striking, in first easily fusing it (at 114° C.), and afterwards converting it (boiling point, 200° C.) into the most exquisitely purple vapour, which is nearly nine times as heavy as air (sp. gr. 8.72), and condenses upon a cool surface in shining scales. Up to 700° C. the sp. gr. of iodine vapour is 127 (H = 1); but, at 1400° the sp. gr. is only about two-thirds of this, indicating a partial decomposition of the molecule. When the vapour is diluted with about four-fifths of its volume of air, its sp. gr. at 1400° is only 63.5 (after allowing for the air), showing that, at this temperature, the molecule is I and not I_2. Iodine stains the skin intensely brown. The specific gravity of solid iodine is 4.95.

When iodine is shaken with cold water, a very small quantity is dissolved (about .05 per cent.), forming a light-brown solution. Hot water dissolves a larger quantity, but alcohol is one of the best solvents for iodine, producing a dark red-brown solution from which part of the iodine may be precipitated by adding water. A solution of potassium iodide also dissolves iodine freely (*Lugol's solution; liquor iodi*). *Tincture of iodine* contains iodine with half its weight of potassium iodide dissolved in alcohol. Benzene and carbon disulphide dissolve it abundantly, producing fine violet-red solutions, which deposit the iodine, if allowed to evaporate spontaneously, in minute rhombic octahedral crystals aggregated into very beautiful fern-like forms. If an extremely weak aqueous solution of iodine be shaken with a little carbon disulphide, the latter will remove the iodine from the solution, and, on standing, will fall to the bottom of the liquid, having a beautiful red colour. By dissolving a large quantity of iodine in carbon disulphide, a solution is obtained which is perfectly opaque to rays of light, though it allows heat-rays to pass freely, and is therefore of great value in physical experiments. A solution of iodine in carbon tetrachloride is also used for the same purpose.

Existing, as iodine does, in very minute quantity in the water from various natural sources, it would often be overlooked if the chemical analyst did not happen to possess a test of the most delicate description for it. Iodine, in the uncombined state, dyes starch of a beautiful blue colour, as may be proved by heating a grain or two of the element with water, and adding to the cold solution a little thin starch (see p. 57), or by placing a minute fragment of iodine in a stoppered bottle, and suspending in it a piece of paper dipped in thin starch. This test, however, though sensitive to the smallest quantity of free iodine, gives no indication whatever with iodine in combination, as it always exists in nature; in order, therefore, to test for iodine, a little starch-paste is added to the suspected liquid, and then a drop of a weak solution of chlorine, which will set free the iodine, and cause the production of the blue colour. It is necessary, however, carefully to avoid adding too much chlorine, since it would immediately destroy the colour of the iodised starch. If, then, a very little sulphurous acid be added, the blue tint returns, and is again bleached by more sulphurous acid.* Alkalies also bleach it, and the colour of a mixture of the iodised starch with water is removed by heating, but returns in great measure when the solution cools. The starch appears to be only dyed by the iodine, and not combined with it; on shaking the blue iodised starch for some time with CS_2, the blue colour is removed, and the red solution of iodine in CS_2 is obtained.

Though very closely connected with chlorine and bromine in its general chemical relations, there are several points in the history of iodine which cause it to stand out in marked contrast by the side of these elements. The attraction which binds it to hydrogen and the metals is certainly weaker than that exerted by chlorine and bromine, so that either of these is capable of displacing it from its compounds, and its bleaching properties are very feeble. Cl, uniting with H, produces 22,000 heat-units; Br produces 13,500, but I *absorbs* 800. Hence HI is much less stable than HBr or HCl. On the other hand, iodine exhibits a more powerful tendency to unite with oxygen; for boiling nitric acid converts it into iodic acid (HIO_3), though this oxidising agent would not affect chlorine or bromine.

Some of the compounds of iodine with the metals are remarkable for their beautiful colours. The *mercuric iodide*, produced by mixing solutions of potassium iodide and mercuric chloride, forms a fine scarlet precipitate, which dissolves in an excess of potassium iodide to a *colourless* solution.

Lead iodide has a bright yellow colour, as may be seen by precipitating potassium iodide with a solution of lead acetate. The precipitate is dissolved by boiling with water (especially on adding a little hydrochloric acid), forming a colourless solution, from which the lead iodide crystallises in very brilliant golden scales on cooling. *Silver iodide* is produced as a yellow precipitate when silver nitrate is added to potassium iodide. The bromide and chloride of silver would form white precipitates. Silver iodide is more stable than the chloride or bromide; when exposed to light it appears to be unchanged, but if a reducing agent, such as ferrous sulphate or pyrogallin, be afterwards poured over it, that portion of the iodide which has been exposed to light is immediately blackened, from the separation of silver in the metallic state. This is the principle of the process for developing the negative photograph taken on a collodion film rendered sensitive by silver iodide. The iodides of potassium, ammonium, and cadmium are also used in photography.

Iodous oxide, I_2O_3, and *iodic oxide*, I_2O_5, are formed when ozone acts upon iodine. Iodous oxide is a yellow, very light powder, which is deliquescent, and is decomposed by water into iodic acid and iodine. It is decomposed suddenly into its elements at 130° C.

126. *Iodic acid*, HIO_3, is most easily prepared by boiling iodine with the strongest nitric acid in a long-necked flask, when it is dissolved

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* The following equations explain these changes:—
(1) $KI + Cl = KCl + I$; (2) $I + 3H_2O + Cl_5 = HIO_3 + 5HCl$;
(3) $2HIO_3 + 5H_2SO_3 = 5H_2SO_4 + I_2 + H_2O$; (4) $I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4$.

in the form of iodic acid, which is left, on evaporating the nitric acid, as a white mass. This may be purified by dissolving in water and crystallising, when the iodic acid forms white hexagonal tables, which have the composition $HIO_3.Aq$. Heated to 266° F. (130° C.) they become HIO_3, and at 360° F. (182° C.) the iodic acid is decomposed into water and iodic anhydride, $2HIO_3 = H_2O + I_2O_5$. This last is decomposed at about 700° F. (371° C.) into iodine and oxygen. The iodic anhydride oxidises combustible bodies, but not with any great violence. The acid is far more stable than chloric and bromic acids. Its solution first reddens litmus-paper, and afterwards bleaches it by oxidation. Its salts, the *iodates*, are less easily soluble in water than the chlorates and bromates, which they resemble in their oxidising action upon combustible bodies. They are all decomposed by heat, evolving oxygen, and sometimes even iodine, showing how much inferior this element is to chlorine and bromine in its attraction for metals. The iodates exhibit some remarkable irregularities in their composition.

Periodic acid, HIO_4, is obtained from the basic sodium periodate formed by passing chlorine through a mixture of sodium iodate and sodium hydrate, when the latter is decomposed, its sodium being abstracted by the chlorine, whilst its oxygen converts the iodic acid into periodic acid; $NaIO_3 + 3NaHO + Cl_2 = 2NaCl + NaIO_4.NaHO.H_2O$ (basic sodium periodate).

This periodate is deposited, being sparingly soluble in water, a most unusual circumstance with sodium salts. By dissolving it in nitric acid, and adding silver nitrate, a basic silver periodate is obtained, which is yellow when precipitated from cold, and red from hot solutions. When the silver salt is dissolved in nitric acid, it is decomposed into silver nitrate, which remains in solution, and normal silver periodate, $AgIO_4$, which is deposited in crystals. When this is boiled with water, it again yields the insoluble basic periodate, and periodic acid is found in the solution. On evaporating the solution, the periodic acid is deposited in prismatic crystals having the composition $HIO_4.2Aq$, which are decomposed at about 320° F.; $2HIO_4.2Aq = I_2O_7 + 3H_2O$. The I_2O_7 is decomposed into I_2O_5 and O_2 at 400° F. The solution of periodic acid, of course, exhibits oxidising properties.

Periodic acid is formed when perchloric acid acts on iodine; $HClO_4 + I = HIO_4 + Cl$. Calcium periodate is precipitated when iodine or potassium iodide is boiled with solution of chloride of lime.

The *periodates* are remarkable for their sparing solubility in water: they are easily decomposed by heat, like the iodates. It will have been remarked in the above account of the preparation of periodic acid, that this acid exhibits a great tendency to the formation of basic salts, whilst iodic acid is remarkable for its acid salts.

There are some reasons for regarding the crystallised periodic acid as $IO(HO)_3(HO)_2$, in which the hydrogen of the two last HO groups only is replaceable by metals, so that the acid is dibasic.

127. *Hydriodic acid* ($HI = 128$ parts by weight = 2 volumes).—Iodine vapour combines with hydrogen, under the influence of heated platinum, to form hydriodic acid gas. The gas is best prepared by decomposing water with iodine in the presence of phosphorus; $6H_2O + I_6 + P_2 = 6HI + 2P(HO)_3$.

100 grains (or 6.5 grms.) of potassium iodide are dissolved in 50 grains (or 3 c.c.) of water in a retort (fig. 182), and 200 grains (or 13 grms.) of iodine are added; when this has dissolved, 10 grains (or 0.65 grm.) of amorphous phosphorus are introduced, and the mixture heated very gradually, the gas being collected by downward displace-

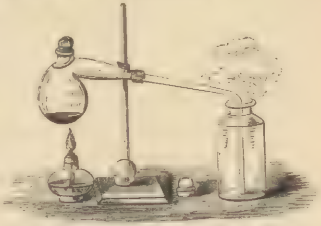

Fig. 182.—Preparation of hydriodic acid.

ment in stoppered bottles, which must be placed in readiness, as the gas comes off very rapidly. These quantities will fill four pint bottles with the gas.

Hydriodic acid gas is very similar in its properties to hydrochloric and hydrobromic acids, fuming strongly in moist air, very readily absorbed by water, liquefied only under strong pressure, and solidified by extreme cold. It is much heavier, its specific gravity being 4.44. If a bottle of hydriodic acid gas be placed in contact with a bottle containing chlorine or bromine vapour diluted with air (fig. 146) it will be instantly decomposed, with separation of the beautiful violet vapour of iodine.

The aqueous solution of hydriodic acid is most conveniently prepared by passing hydrosulphuric acid gas through water in which iodine i suspended, $H_2S + I_2 = 2HI + S$, the separated sulphur being filtered off, and the solution boiled to expel the excess of hydrosulphuric acid. By this method, it is not possible to obtain a solution of HI of greater sp. gr. than 1.56 (whereas the strongest is 1.99). for the reaction stops when the heat produced by the absorption of the gas by water is just equal to the heat *absorbed* in the formation of HI. Strong solution of hydriodic acid converts sulphur into H_2S. Solution of hydriodic acid differs greatly from hydrochloric and hydrobromic acids, in being decomposed by exposure to air, its hydrogen being oxidised and iodine separated, which dissolves in the liquid, and renders it brown.

This tendency of the hydrogen of hydriodic acid to combine with oxygen renders that acid a powerful *reducing* agent. It is even capable of converting sulphuric acid into hydrosulphuric acid—

$$H_2SO_4 + 8HI = H_2S + 4H_2O + I_8,$$

so that when potassium iodide is heated with concentrated sulphuric acid, hydrosulphuric acid is evolved in considerable quantity.

The action of hydriodic acid upon the metals and their oxides is generally similar to that of the other hydrogen acids. In organic chemistry, hydriodic acid is often employed for removing oxygen and replacing it by hydrogen.

When potassium is heated in a measured volume of gaseous hydriodic acid, the iodine is removed, and the hydrogen occupies half the original volume. Hence 1 volume of hydrogen is combined with 1 volume of iodine vapour in 2 volumes of hydriodic acid.

Like chlorine and bromine, iodine is capable of displacing hydrogen from many organic compounds, and of taking its place; but its action in this respect is much feebler. The circumstance that the organic compounds containing iodine are generally much less volatile, and therefore more manageable, than those of chlorine and bromine, leads to the extensive employment of this element in researches upon organic substances.

With olefiant gas, iodine forms a crystalline solid compound ($C_2H_4I_2$) corresponding to Dutch liquid (p. 96).

Carbon tetra-iodide, CI_4, is obtained by decomposing carbon tetrachloride with aluminium iodide, in presence of carbon disulphide. It forms octahedral crystals which are very unstable.

128. *Iodide of nitrogen.*—The action of chlorine, bromine, and iodine upon ammonia exemplifies the difference in their attraction for hydrogen; for whilst chlorine and bromine, acting upon ammonia, cause

the liberation of a certain amount of nitrogen, iodine simply removes two-thirds of the hydrogen, and itself fills up the vacancies thus occasioned, no nitrogen being liberated, $NH_3 + I_4 = NHI_2 + 2HI$, the hydriodic acid thus formed combining with more ammonia to form ammonium iodide.

To prepare the iodide of nitrogen, 20 grains (or 1.3 grm.) of iodine are rubbed to powder in a mortar and mixed with half a fluid ounce (or 14 c.c.) of strong ammonia: the mortar is covered with a glass plate, and after about half an hour the iodide of nitrogen is collected in separate portions upon four filters, which are allowed to drain and spread out to dry. The brown solution contains iodine dissolved in ammonium iodide.

Another method consists in dissolving iodine in a mixture of hydrochloric with a little nitric acid, with the aid of heat, and adding ammonia, which decomposes the ICl in solution, and gives a black precipitate of the iodide of nitrogen.

The iodide is a black powder, which explodes with a loud report even when touched with a feather, emitting fumes of hydriodic acid and purple vapour of iodine: its explosion is probably represented by the equation $NHI_2 = N + HI + I$, its violence being accounted for by the sudden evolution of a large volume of gas and vapour from a small volume of solid. Even when allowed to fall from the height of a few feet upon the surface of water, it explodes if perfectly dry. In the moist state it slowly undergoes decomposition.

When dry NH_3 gas is passed over iodine cooled by ice, *iodammonium iodide*, $(NH_3I)I$, is produced.

129. Iodine forms two compounds with chlorine, *monochloride* (ICl) and *trichloride* (ICl_3). The former is obtained by distilling 1 part of iodine with 4 parts of potassium chlorate, as a brown liquid which is reluctant to solidify, though it then fuses at 24° C. and boils at 101° C.

The trichloride forms fine red needle-like crystals, and is produced when iodine or hydriodic acid gas is acted upon with an excess of chlorine. ICl_4 has been obtained in red octahedra by the spontaneous decomposition of ICl. The chlorides of iodine are decomposed by water, yielding HIO_3, HCl, and iodine. From the aqueous solution of ICl, ether extracts a yellow volatile compound having the composition ICl.HCl.

Iodine bromide, IBr, is a crystalline solid resembling iodine, fusing at 36° C. and subliming with partial decomposition. Water decomposes it, iodine being separated.

FLUORINE.

F = 19 parts by weight.

130. The most ornamental mineral substance occurring in any abundance in this country is known as *fluor spar* or *Derbyshire spar* (fluoride of calcium), and is found with several beautiful shades of colour—blue, purple, violet, or green, and sometimes perfectly colourless, either in large masses or in crystals, which have the form of a cube or of some solid derived from it. The use of this mineral as a flux in smelting ores dates from a very remote period, and from this use the name fluor appears to have been originally derived; but we have no record of its chemical examination till about a century since, when Margraf found his glass retort powerfully corroded in distilling this mineral with sulphuric acid, and Scheele soon after announced that it contained lime and *fluoric acid*. But though this chemist had fallen into the error to which analysts

are continually liable, of mistaking products for educts, his experiments, as they were afterwards perfected by Gay-Lussac and Thénard, deserve particular consideration.

131. *Hydrofluoric acid* ($HF = 20$ parts by weight = 2 volumes).*—If powdered fluor spar be mixed with twice its weight of oil of vitriol, and heated in a leaden retort (fig. 183), the neck of which fits tightly into a leaden condensing-tube, cooled in a mixture of ice and salt, a colourless liquid distils over, and the residue in the retort is found to consist of calcium sulphate;† $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. The colourless liquid (hydrofluoric acid) possesses most remarkable properties; it is powerfully acid, fumes strongly in the air, and has a most pungent irritating odour. If the air is at all warm, the liquid begins to boil when taken out of the freezing mixture. Should the operator have the misfortune to allow a drop to fall upon his hand, it will produce a very painful sore, even its vapour producing pain under the finger nails. Its attraction for water is so great, that the acid hisses like red-hot iron when brought in contact with it. But its most surprising property is that of rapidly corroding glass, which has already been alluded to as noticed by Margraf. Experiment soon proved that great analogy existed between the properties of this new acid and those of hydrochloric acid; and Ampère was led to believe that the acid was a hydrogen-acid, containing a new salt radical, which he named fluorine; the name of the acid was then changed from fluoric to hydrofluoric acid.

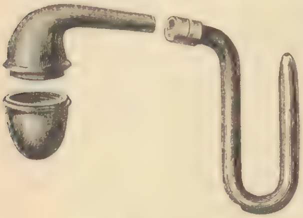

Fig. 183.

This liquid has since been proved to be a solution of hydrofluoric acid in water; for if it be distilled with phosphoric anhydride, which retains the water, it evolves hydrofluoric acid gas, which resembles hydrochloric acid gas in fuming strongly on contact with moist air and being eagerly absorbed by water, but has a far more pungent odour.

Pure hydrofluoric acid is prepared by heating dry *potassium hydrofluate* (KHF_2) to redness in a platinum still. It is then obtained as a colourless liquid, which boils at 67° F. (19° C.), and has the specific gravity 0.988 at 55° F. It solidifies at $-102°$ C. and melts again at $-92°$. The pure acid scarcely affects metals, excepting potassium and sodium. It corrodes glass, however, rapidly, though its vapour has little action on glass unless moisture is present. It combines eagerly with sulphuric and phosphoric anhydrides, with great evolution of heat, a circumstance in which it resembles water, and differs altogether from its more obvious analogue, hydrochloric acid. It is also found that it combines energetically with the fluorides of potassium and sodium, precisely as water combines with the oxides of those metals.

It is remarkable that the solution of hydrofluoric acid, in its concentrated form, is not so heavy as a somewhat weaker acid. Thus the acid of sp. gr. 1.06 acquires the sp. gr. 1.15 on addition of a little water; but on adding more water, its sp. gr. is again reduced. It would hence appear that the acid of 1.15 is a definite hydrate of hydrofluoric acid; its composition corresponds to $HF.2H_2O$. It distils unchanged at 248° F. (120° C.). The solution is generally kept in bottles made of gutta-percha.

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* From some determinations of the specific gravity of the vapour at low temperatures, Mallet considers the molecule to be $H_2F_2 = 40$, and to undergo dissociation into $2HF$ at temperatures approaching 100° C.

† The mineral kryolite (fluoride of aluminium and sodium) may be advantageously substituted for fluor spar, being more easily obtained in a pure state. For preparing the acid on a large scale, iron retorts are employed.

The action of hydrofluoric acid upon metals and their oxides resembles that of hydrochloric acid. It dissolves all ordinary metals except gold, platinum, silver, mercury, and lead. Strange to say, it has but little action on magnesium.

The property which renders this acid so useful to the chemist is its power of dissolving silica even in its most refractory form. When sand or flint reduced to powder is digested in a leaden or platinum vessel with hydrofluoric acid, it is gradually dissolved; and if the solution be evaporated, the whole of the silica will be found to have disappeared in the form of gaseous silicon tetrafluoride; $SiO_2 + 4HF = SiF_4 + 2H_2O$. If the silica be combined with a base, the metal will be left as a fluoride, decomposable by sulphuric or hydrochloric acid. This renders hydrofluoric acid a most valuable agent in the analysis of the numerous mineral silicates which resist the action of other acids.

The corrosion of glass by hydrofluoric acid is now easily explained. Ordinary glass consists of silicate of sodium or potassium combined with silicate of calcium or lead. The hydrofluoric acid attacks and removes the silica, and thus eats its way into the glass.

In order to demonstrate the action of this acid upon glass, a glass plate is warmed sufficiently to melt wax, a piece of which is then rubbed over it, until the glass is covered with a thin and pretty uniform coating. Upon this a word or drawing may be engraved with a sharp point so that the lines shall expose the glass. A mixture of powdered fluor spar with concentrated sulphuric acid is then poured over it, and allowed to remain for a quarter of an hour; the acid mixture is washed off, and the plate gently warmed to melt the wax, which may be wiped off with a little tow, when it will be found that the hydrofluoric acid evolved from the mixture has corroded those portions of the glass from which the graver had removed the wax. It has been attempted to apply this process to the production of engravings, but the brittleness of the plate has formed a very serious obstacle.

If a leaden or platinum dish be at hand, it is better to place the glass to be etched over the dish containing the mixture of fluor spar and sulphuric acid exposed to a very gentle heat.

The solution of hydrofluoric acid etches glass without deadening the surface, as is the case with the vapour; but a solution of fluoride of potassium or ammonium mixed with sulphuric acid does produce a dead surface, and is much used for engraving on glass. An ink sold for writing on glass with a steel pen is composed of barium and ammonium fluorides and sulphuric acid.

132. *Fluorine isolated.*—Many ingenious experiments have been made in order to obtain fluorine in the separate state, but it was found that it invariably combined with some portion of the material of the vessel in which the operation was conducted. The most successful of the early attempts to isolate fluorine appears to have been made, at the suggestion of Davy, in a vessel of fluor spar itself, which could not, of course, be supposed to be in any way affected by it. At last, fluorine has been obtained in the pure state by decomposing hydrofluoric acid by the galvanic current. The acid having been very carefully obtained pure, a little potassium hydrofluoride was dissolved in it to improve its conducting power, and it was subjected to the action of the current in

a **U**-tube of platinum, down the limbs of which the electrodes were inserted; the negative electrode was a rod of platinum, and the positive was made of an alloy of platinum with 10 per cent. of iridium. The **U**-tube was provided with stoppers of fluor spar and platinum delivery tubes for the gases, and was cooled to −23° C. The gaseous fluorine which was extricated at the positive electrode was colourless, and possessed the properties of chlorine, but much more strongly marked. It decomposed water immediately, seizing upon its hydrogen, and liberating oxygen in the ozonised condition; it exploded with hydrogen, even in the dark, and combined, with combustion, with most metals and non-metals, even with boron and silicon in their crystallised modifications. Carbon, however, was not attacked by it.

Fluorides.—Solutions of the fluorides of potassium and the other alkali metals corrode glass slowly, like hydrofluoric acid. The fluorides are capable of combining with the acid; thus potassium fluoride forms $KF.HF$, which, when dry, is a convenient source of hydrofluoric acid gas when moderately heated. The only fluoride possessed of much practical interest beside the fluoride of calcium, is the mineral *kryolite* (κρύος, *frost*), which is a double fluoride of aluminium and sodium (Na_3AlF_6), found abundantly in Greenland, and valuable as a source of aluminium and soda. The *topaz* contains fluorine, but in what form of combination is not certain; its other constituents are alumina and silica. *Tourmaline* also contains fluorine, together with alumina, silica, and FeO. In such minerals it is probable that the fluorine replaces part of the oxygen.

Magnesium fluoride (MgF_2) forms the mineral *Sellaite* which is found, crystallised, in Savoy. Fluorides are also found, though in very small quantity, in sea water, and they have been discovered in plants and animals. Human bone contains about 2 per cent. of calcium fluoride.

No compound of fluorine with oxygen is known.

133. *Silicon tetrafluoride* (SiF_4 = 104 parts by weight = 2 volumes).—If a mixture of powdered fluor spar and glass be heated, in a test-tube or small flask, with concentrated sulphuric acid, a gas is evolved which has a very pungent odour, and produces thick white fumes in contact with the air*: it might at first be mistaken for hydrofluoric acid, but if a glass rod or tube be moistened with water and exposed to the gas, the wet surface becomes coated with a white film, which proves, on examination, to be silica. This result originated the belief that the gas consisted of fluoric (now hydrofluoric) acid and silica; but Davy corrected this view by showing that it really contained no oxygen, and consisted solely of silicon and fluorine. The gas is now called silicon tetrafluoride, and represents silica in which the oxygen has been displaced by fluorine: the change of places between these two elements in the above experiment is represented by the subjoined equation—

$$\underset{\substack{\text{Fluor}\\\text{spar.}}}{2CaF_2} + \underset{\text{Silica.}}{SiO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{2CaSO_4} + \underset{\substack{\text{Silicon}\\\text{tetrafluoride.}}}{SiF_4} + 2H_2O.$$

The formation of the crust of silica upon the wetted surface of the glass is due to a decomposition which takes place between the tetrafluoride and the water, in which the oxygen and fluorine again change places; $SiF_4 + 2H_2O = SiO_2 + 4HF$. Since this latter equation shows that hydrofluoric acid is again formed, it would be expected that the glass beneath the deposit of silica would be found corroded by the acid; this, however, is not the case, and when the experiment is repeated upon a somewhat larger scale, so that the water which has acted upon the gas may be examined, it will be found to hold in solution, not hydrofluoric acid, but an acid which has little action upon glass, and is composed of hydrofluoric acid and silicon fluoride, so that the hydrofluoric acid produced when water acts upon the fluoride, combines with a portion of the latter to produce the new acid $2HF.SiF_4$, or H_2SiF_6, *hydrofluo-silicic acid.*

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* SiF_4 becomes solid at −102° C., and, at a higher temperature, evaporates without fusing.

For the preparation of silicon tetrafluoride, 1 oz. (or 30 grms.) of fluor spar and an equal weight of powdered glass are mixed together, and heated in a Florence flask, with 7 oz. (measured) (or 200 c.c.) of oil of vitriol, the gas being collected in dry bottles by downward displacement (see fig. 169, p. 155). If a little of the gas be poured from one of the bottles into a flask filled up to the neck with water, the surface of the latter will become covered with a layer of silica, so that if the flask be quickly inverted, the water will not pour from it, and will seem to have been frozen. In a similar manner, a small tube filled with water and lowered into a bottle of the gas, will appear to have been frozen when withdrawn. A stalactite of silica some inches in length may be obtained by allowing water to drip gently from a pointed tube into a bottle of the gas. Characters written on glass with a wet brush are rendered opaque by pouring some of the gas upon them.

134. *Hydrofluo-silicic acid*, or *silico-fluoric acid* (H_2SiF_6 = 144 parts by weight).—This acid is obtained in solution by passing silicon tetrafluoride into water; $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$.

The gas must not be passed directly into the water, lest the separated silica should stop the orifice of the tube, to prevent which the latter should dip into a little mercury at the bottom of the water, when each bubble, as it rises through the mercury into the water, will become surrounded with an envelope of gelatinous silica, and if the bubbles be very regular, they may even form tubes of silica extending through the whole height of the water.

Crystals of $H_2SiF_6.2Aq$ have been obtained by passing SiF_4 into solution of HF.

For preparing hydrofluo-silicic acid, it will be found convenient to employ a gallon stoneware bottle (fig. 184), furnished with a wide tube dipping into a cup of mercury placed at the bottom of the water. 1 lb. (or 500 grms.) of finely powdered fluor spar, 1 lb. of fine sand, and 64 measured ounces (or 2 litres) of oil of vitriol are introduced into the bottle, which is gently heated upon a sand-bath, the gas being passed into about 5 pints (or 3 litres) of water. After six or seven hours the water will have become pasty, from the separation of gelatinous silica. It is poured upon a filter, and when the liquid has drained through as far as possible, the filter is wrung in a cloth, to extract the remainder of the acid solution, which will have a sp. gr. of about 1.078.

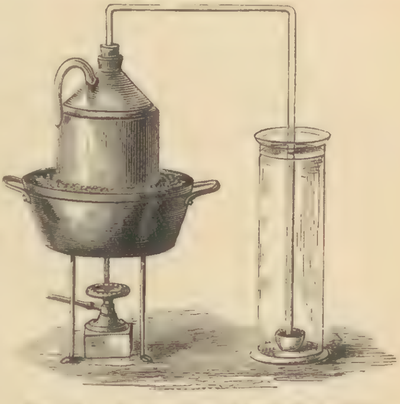

Fig. 184.—Preparation of hydrofluo-silicic acid.

A dilute solution of hydrofluo-silicic acid may be concentrated by evaporation up to a certain point, when it begins to decompose, evolving fumes of silicon tetrafluoride, hydrofluoric acid remaining in solution and volatilising in its turn if the heat be continued. Of course the solution corrodes glass and porcelain when evaporated in them. If the solution of hydrofluo-silicic acid be neutralised with potash, and stirred, a very characteristic crystalline precipitate of potassium silico-fluoride is formed—

$$H_2SiF_6 + 2KHO = K_2SiF_6\ (\textit{Potassium silico-fluoride}) + 2H_2O.$$

But if an excess of potash be employed, a precipitate of gelatinous silica will be separated, potassium fluoride remaining in the solution—

$$H_2SiF_6 + 6KHO = 6KF + 4H_2O + SiO_2.$$

One of the chief uses of hydrofluo-silicic acid is to separate the potassium from its combination with certain acids, in order to obtain these in the separate state.

Si_2F_6 is a solid obtained by passing SiF_4 gas over fused silicon.

135. *Boron trifluoride* (BF_3) may be prepared by a process similar to that employed for silicon fluoride, but it is also obtained by strongly heating a mixture of powdered boric anhydride with twice its weight of fluor spar in an iron tube; $3CaF_2 + B_2O_3 = 3CaO + 2BF_3$.

The boron fluoride is a gas which fumes strongly in moist air, like the silicon fluoride. It is absorbed eagerly by water, with evolution of heat. One volume of water at 0° C. is capable of dissolving 1057 volumes of boron fluoride, producing a corrosive heavy liquid (sp. gr. 1.77), which fumes in air, and chars organic substances on account of its attraction for water. This solution is known as *fluoboric* or *borofluoric acid*, and its formation is explained by the equation—

$$2BF_3 + 3H_2O = B_2O_3.6HF\ (\textit{Fluoboric acid}).$$

When the solution is heated, it evolves boron fluoride, until its specific gravity is reduced to 1.58, when it distils unchanged.

Hydrofluoboric acid is obtained in solution by adding a large quantity of water to fluoboric acid; $2(B_2O_3.6HF) = H_3BO_3 + 3H_2O + 3HBF_4$ (*Hydrofluoboric acid*

This acid resembles the hydrofluo-silicic; its hydrogen may be exchanged for metals to form *borofluorides*.

136. *General review of chlorine, bromine, iodine, and fluorine.*—These four elements compose a natural group, the members of which are connected by the similarity of their chemical properties far more closely than those of any other group of elements. They are usually styled the *halogens*, from their tendency to produce salts resembling sea salt in their composition (ἅλς, *the sea*), and such salts are called *haloid salts*. These elements are also called *salt-radicals*, from their property of forming salts by direct union with the metals. Each of these elements is monatomic, and combines with an equal volume of hydrogen to form an acid which occupies the joint volumes of its constituents.

The halogens also supply the most prominent example of the gradation in properties sometimes observed among the members of the same natural group of elements.

In the order of their chemical energy, that is, of the force with which they hold other elements in chemical combination with them, fluorine should stand first, its combining energy being so great as to cause a serious difficulty in isolating it; chlorine would rank next, then bromine, and iodine last.

The atomic weights follow the inverse order of their chemical energies: fluorine, 19; chlorine, 35.5; bromine, 80; iodine, 127—numbers which, of course, also represent their relative specific gravities in the state of vapour.

A similar gradation is observed in their physical state and colour, fluorine being a colourless gas, chlorine a yellow gas, bromine a red liquid boiling at 63° C., and iodine a black solid boiling at 200° C.

Even in the exceptions which occur to the order of chemical energy above alluded to, the same progression is noticed: thus fluorine has so little attraction for oxygen that no oxide is known; chlorine has less attraction for oxygen than bromine (chloric acid being less stable than bromic), whilst bromine has less than iodine, which is capable even of uniting directly with ozonised oxygen.

The compounds of these elements with hydrogen are all gases distinguished by a powerful attraction for moisture and great similarity of odour.

Their potassium salts all crystallise in the same (cubical) form.

The silver fluoride is deliquescent and soluble in water; the chloride is insoluble in water, but dissolves very easily in ammonia; the bromide dissolves with some difficulty in ammonia; and the iodide is insoluble. In some other particulars, fluorine stands apart from the other halogens; thus the fluoride of calcium is a very insoluble substance, whilst the chloride, bromide, and iodide are very soluble.

Hydrofluoric acid forms KHF_2, which corresponds in composition to KHO.

SULPHUR.

S = 32 parts by weight = 1 volume (at 1000° C.).

137. Sulphur is remarkable for its abundant occurrence in nature in the uncombined state, in many volcanic districts. It is also found, as sulphuretted hydrogen, in many mineral waters, and very abundantly in combination with metals, forming the numerous ores known as *sulphurets* or *sulphides*, of which the following are the most abundant:—

Iron pyrites,	Iron disulphide,	FeS_2
Copper pyrites,	Sulphide of iron and copper,	$Cu_2S.Fe_2S_3$
Galena,	Sulphide of lead, ..	PbS
Blende,	Sulphide of zinc,	ZnS
Crude antimony,	Sulphide of antimony,	Sb_2S_3
Cinnabar,	Sulphide of mercury,	HgS.

Sulphur is plentifully distributed also, in combination with oxygen and a metal, in the form of *sulphates*, of which the most conspicuous are—

Gypsum,	Sulphate of calcium,	$CaSO_4.2H_2O$
Heavy spar,	Sulphate of barium,	$BaSO_4$
Celestine,	Sulphate of strontium,	$SrSO_4$
Epsom salts,	Sulphate of magnesium,	$MgSO_4.7H_2O$
Glauber's salt,	Sulphate of sodium,	$Na_2SO_4.10H_2O$.

In plants, sulphur is also found in the form of sulphates, and as a constituent of the vegetable albumen (of which it forms about 1.5 per cent.) present in the sap. It is also contained in certain of the essential oils remarkable for their peculiar pungent odour, such as those of garlic and mustard.

In animals, sulphur occurs as sulphates, as a constituent of albumen, fibrin, and casein (in neither of which does it exceed 2 per cent.); and in bile, one of the products from which, taurine, contains 25 per cent. of sulphur.

For our supplies of sulphur we are chiefly indebted to Sicily, where large quantities of it are found in an uncombined state in beds of blue clay. Magnificent crystalline masses of strontium sulphate are often found associated with it; the sulphur itself sometimes occurs in the form of transparent yellow octahedra, but more frequently in opaque amorphous masses. The districts in which sulphur is found are usually volcanic, and those which border the Mediterranean are particularly rich in it. Sulphur has also been found in Iceland and California.

The *native* sulphur being commonly distributed in veins through masses of gypsum and celestine, has to be separated from these by the action of heat. When the ores contain more than 12 per cent. of sulphur, the bulk of it is melted out, the ore being thrown into rough furnaces or cauldrons with a little fuel, and smothered up with earth, so as to prevent the combustion of the sulphur, which runs down in the liquid state to the bottom of the cauldron, and is drawn out into wooden moulds.* But when the proportion of sulphur is small, the ore is heated so as to convert the sulphur into vapour, which is condensed in another vessel. The operation is conducted in rows of earthen jars (A, fig. 185) heated in a long furnace, and provided with short lateral pipes, which convey the sulphur into similar jars (B) standing outside the furnace, in which the vapour of sulphur condenses in the liquid

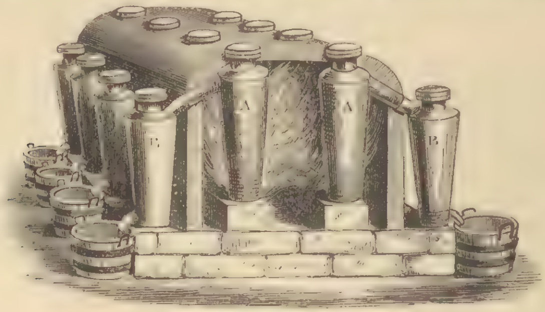

Fig. 185.—Distillation of sulphur.

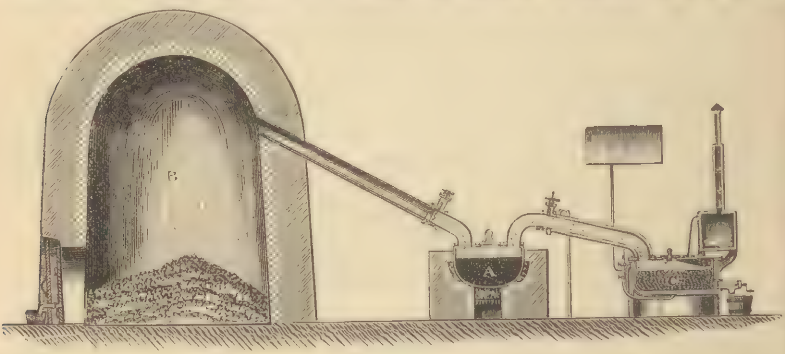

Fig. 186.—Sulphur refinery.

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* High pressure steam has been applied with advantage for melting the sulphur out of the ores, which are enclosed in an iron vessel; or the ores are heated in a boiler with a 66 per cent. solution of calcium chloride at 120° C. The sulphur is sometimes extracted by dissolving it with carbon disulphide. When sulphur ores containing calcium sulphate are distilled, part of the sulphur is lost as sulphur dioxide, which goes off as gas—

$$CaSO_4 + S_2 = CaS + 2SO_2.$$

state, and flows out into pails of water. The sulphur obtained by this process is imported as *rough sulphur*, and contains 3 or 4 per cent. of earthy impurities. In order to separate these, it is redistilled, in this country, in an iron retort (A, fig. 186), from which the vapour is conducted into a large brick chamber (B), upon the sides of which it is deposited in the form of a pale yellow powder (*flowers of sulphur*, or *sublimed sulphur*). When the operation has been continued for some time, the walls of the chamber become sufficiently hot to melt the sulphur, which is allowed to collect, and afterwards cast in wooden moulds, forming *roll sulphur* or *brimstone*. *Distilled sulphur* is obtained by allowing the vapour to pass from the retort into a small receiving-vessel (C) cooled by water, where it condenses in the liquid state: this variety of sulphur is preferred for the manufacture of gunpowder, for reasons which will be stated hereafter.

Sulphur is readily distilled on a small scale in a Florence flask (fig. 187), another flask cut off at the neck being employed as a receiver. The flask containing the sulphur should be supported upon a thin iron wire triangle, and heated by a gauze burner, at first gently, and afterwards to the full heat. Flowers of sulphur will at first condense in the receiver, and will be followed by distilled sulphur when the temperature increases. A slight explosion of the mixture of sulphur vapour and air may take place at the commencement of the distillation. An ounce of sulphur may be distilled in a few minutes.

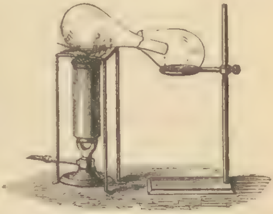

Fig. 187.—Distillation of sulphur.

We are by no means entirely dependent upon Sicily for sulphur, for this element can be easily extracted from iron and copper pyrites, both of which are found abundantly in this country.

Iron pyrites forms the yellow metallic-looking substance which is often met with in masses of coal, sometimes in distinct cubical crystals, and which is to be picked up in large quantities on some sea-beaches, where it occurs in rounded nodules, rusty outside, but having a fine radiated metallic fracture. When this mineral is strongly heated, it gives up part of its sulphur; at a very high temperature one-half of the sulphur may be separated, $FeS_2 = FeS + S$, but by an ordinary furnace heat only about one-fourth can be obtained. The distillation of iron pyrites is sometimes effected in conical fireclay vessels (fig. 188) closed at the wider end, and stopped towards the other with a perforated plate, to allow the passage of the sulphur vapour. Each vessel contains 100 lbs. of pyrites, and yields 14 lbs. of sulphur.

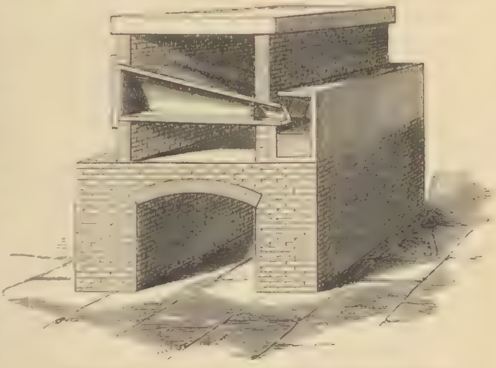

Fig. 188.—Furnace for distillation of sulphur from pyrites.

The sulphur obtained in this way has a green colour, due to the presence of a little sulphide of iron carried over mechanically during the distillation: in order to purify it, it is melted and allowed to cool slowly, when the sulphide of iron subsides: the upper portion of the mass is then further purified by distillation.

Sulphur may also be obtained from copper pyrites ($Cu_2S.Fe_2S_3$) in the process of roasting the ore, previously to the extraction of the copper. The ore is heaped up into a pyramid, the base of which is about 30 feet square: a layer of powdered ore is placed at the bottom, to prevent too rapid access of air: above this there is a layer of brushwood: a wooden chimney is placed in the centre, and is made to communicate with air-passages left between the faggots: around this chimney the large fragments of the ore are piled to a height of about 8 feet, and a layer of powdered ore, about 12 inches deep, is strewn over the whole. The heap contains about 2000 tons of pyrites, and will yield 20 tons of sulphur. The fire, being kindled by dropping lighted faggots down the chimney, burns very slowly, because of the limited access of air, and after a few days sulphur is seen to exude from the surface, and is received in cavities made for the purpose in different parts of the heap. The roasting requires five or six months for its completion. In this operation a part of the sulphur has been separated by the mere action of heat, and another part has been displaced by the oxygen of the air, which has converted a portion of the iron into an oxide. A part of the separated sulphur has been burnt, the rest having escaped combustion on account of the limited access of air.

The sulphur extracted from pyrites is generally found to contain a little arsenic, which is frequently associated with those minerals. Immense quantities of sulphur are consumed in this country for the manufacture of sulphuric acid, gunpowder, lucifer matches, vulcanised caoutchouc, and for making the sulphurous acid gas employed in bleaching processes.

Much sulphur has recently been extracted from the *tank-waste* of the alkali works, by a process which will be described in the manufacture of carbonate of soda.

138. *Properties of sulphur.*—In its ordinary forms sulphur has a characteristic yellow colour, though *milk of sulphur*, or precipitated sulphur (obtained by adding an acid to the solution of sulphur in an alkali), is white. It suffers electrical disturbance with remarkable facility, so that when powdered in a dry mortar it clings to it with great pertinacity.

Finely divided sulphur, especially sublimed sulphur, is gradually oxidised and converted into sulphuric acid when exposed to moist air.

One of the most remarkable features of sulphur is its inflammability, due to its tendency to combine with oxygen at a moderately elevated temperature. It melts at 115° C. (239° F.), and inflames at about 260° C. (500° F.), burning with a pale blue flame, and emitting the well-known suffocating odour of sulphurous acid gas (SO_2). The changes in the physical condition of this element under the influence of heat are very extraordinary. If a quantity of sulphur be introduced into a Florence flask and subjected to a gradually increasing heat (fig. 189), it is soon converted into a pale yellow limpid liquid (120° C.), the colour of which becomes gradually brown as the temperature rises, until, at about 180° C., it is nearly black and opaque, and is so viscid that the flask may be inverted without spilling it: at this point the temperature of the sulphur remains stationary for a time, notwithstanding that it is still over the flame, showing that heat is becoming latent in converting the sulphur into the new modification. On continuing the heat the sulphur once more becomes liquid at 260° C., though not so mobile as at first, and at a much higher temperature, 444° C. (836° F.), it boils, and is converted into a brownish red, very heavy vapour: at this point of the experiment an explosion of the mixture of sulphur vapour with air often takes place. The flask may now be removed from the flame, and a little of the sulphur poured into a vessel of water, through which it will descend in a continuous stream, forming a soft elastic string like india-rubber: the portion remaining in the flask will be observed, as it cools, to pass again through the same states, becoming viscid at 180° C., and very liquid at 120° C.; another portion may now be poured into water, through which it will fall in isolated drops, solidifying into yellow brittle crystalline buttons of ordinary sulphur. As the portion of sulphur left in the flask cools, it will be found to deposit small tufts of crystals, and ultimately to solidify altogether to a yellow crystalline mass.

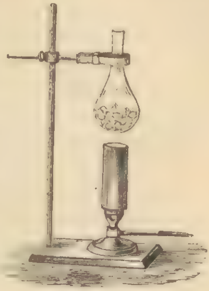

Fig. 189.

The brown *ductile sulphur*, when kept for a few hours, will become yellow and brittle, passing, in great measure, spontaneously into the crystalline sulphur. The change is accelerated by a gentle heat, and is attended with evolution of the heat which the sulphur was found to absorb at 180° C. Both these varieties of sulphur are of course insoluble in water, and they are not dissolved to any great extent by alcohol and ether; but these, when heated, will dissolve enough to be deposited in *white* silvery needles on cooling. Glacial acetic acid also dissolves sulphur, and deposits it in needles. If the crystalline variety be shaken with a little carbon disulphide, it rapidly dissolves, and on allowing the solution to evaporate spontaneously, it deposits beautiful octahedral crystals, resembling those of native sulphur (fig. 190). Ductile sulphur, however, is insoluble in carbon disulphide.

When flowers of sulphur are shaken with carbon disulphide, a considerable quantity passes into solution, the remainder consisting of the *amorphous*, or insoluble sulphur. Roll sulphur dissolves to a greater extent, and sometimes entirely, in the disulphide, and distilled sulphur is always easily soluble.

The soluble and insoluble forms of sulphur appear to represent distinct chemical varieties of the element. When a solution of hydric sulphide (H_2S) is decomposed by the galvanic battery, the hydrogen, as would be expected, is separated at the negative pole, and the sulphur at the positive pole (p. 11). The sulphur, therefore, was the *electro-negative* element of the compound. This sulphur is soluble in carbon disulphide. When an acid is added to a solution of an alkaline sulphide containing more than one atom of sulphur, the excess of the latter is precipitated, and is then also found to be soluble in carbon disulphide; for it played an electro-negative part towards the metal with which it was in combination.

When sulphurous acid is decomposed by the battery, the sulphur is separated at the negative pole, showing that it played an *electro-positive* part in the sulphurous acid. This electro-positive sulphur is insoluble in carbon disulphide. The sulphur in the chloride of sulphur (S_2Cl_2) also plays an electro-positive part, and accordingly when this compound is decomposed by water, the sulphur which separates is insoluble in carbon disulphide. The existence of these two forms of sulphur affords some support to the theory of the dual constitution of the elements noticed at p. 56. When a beam of solar light is thrown by a lens through a solution of sulphur in carbon disulphide, a precipitation of insoluble sulphur takes place in the track of the beam.

The electro-positive sulphur would be expected to manifest a greater attraction for oxygen than the electro-negative variety, and accordingly it is found to be far more easily oxidised by nitric acid. Electro-positive or insoluble sulphur is converted into electro-negative or soluble sulphur by the action of a moderate heat, itself evolving heat during the process of conversion: when melted in contact with sulphurous acid gas, the soluble sulphur is converted externally into the insoluble form.

Crystalline or soluble sulphur is capable of existing in two distinct forms. The natural form of crystallised sulphur is derived from the octahedron with a rhombic base (fig. 190), and it is a modification of this form which sulphur assumes when crystallised from its solutions. But if sulphur be melted in a covered crucible, allowed to cool until the surface has congealed, and the remaining liquid portion poured out after piercing the crust (with two holes, one for admission of air), the crucible will be lined with beautiful needles, which are derived from an oblique prism (fig. 191). These crystals are brownish-yellow and transparent, when freshly made, but they soon become opaque yellow; and although they retain their prismatic appearance, they have now changed into minute rhombic octahedra, the change being attended with evolution of heat.* On the other hand, if a crystal of octahedral sulphur be exposed for a short time to a temperature of about 230° F. (110° C.), in a boiling saturated solution of common salt, for example, it becomes opaque, in consequence of the formation of a number of minute prismatic crystals in the mass.

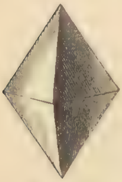

Fig. 190.

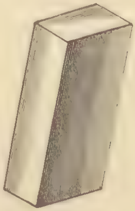

Fig. 191.

Both crystalline forms of sulphur may be obtained at the same temperature from *superfused* sulphur, or from a supersaturated solution of sulphur in benzene, by dropping in a crystal of the form required.

The difference between these two forms of crystalline sulphur extends to their fusing points and specific gravities, the prismatic sulphur fusing at 248° F. (120° C.), and the octahedral sulphur at 239° F. (115° C.), the specific gravity of the prisms being 1.98, and that of the octahedra 2.05.

Roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but after being kept for some time, it consists of octahedra, although the mass generally retains the specific gravity proper to the prismatic form. This change in the structure of the mass, taking place when its solid condition prevented the free movement of the particles, gives rise to a state of tension which may account for the extreme brittleness of roll sulphur. If a stick of sulphur be held in the warm hand, it often splits, from unequal expansion. These peculiarities of sulphur deserve careful study, as helping to elucidate the spontaneous alterations in the structure of glass, iron, &c., under certain conditions.

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* Spring has shown that a pressure of 6000 atmospheres converts prismatic sulphur and plastic sulphur into the octahedral variety.

Flowers of sulphur do not present a crystalline structure, but consist of spherical granules composed of insoluble sulphur enclosing soluble sulphur. Hot oil of turpentine dissolves sulphur freely, and when the solution is allowed to stand, the crystals which are deposited whilst the solution is hot have the prismatic form, but as it cools, octahedra are separated.

The following table exhibits the chief *allotropic* forms of sulphur:—

	Sp. gr.	Fusing point.	In Carbon Disulphide.
Octahedral Electro-negative	2.05	115° C.	Soluble.
Prismatic	1.98	120°	Soluble.
Ductile Amorphous Electro-positive	1.96	Becomes octahedral.	Insoluble.

The octahedral is by far the most stable of the three, and is the ultimate condition which the others assume.

Other varieties of sulphur, such as a black and a red modification, have been described, but they are of minor importance.

Sulphur is capable of entering into direct combination with several other elements. It unites with chlorine and with some of the metals, if finely divided, even at the ordinary temperature, and it is capable of combining at a high temperature with all the non-metals except nitrogen, and with nearly all the metals.

A mixture of 5 parts of iron-powder (*ferrum redactum*) and 3 parts of flowers of sulphur will burn when kindled by a match, leaving a black mass of ferrous sulphide. Zinc-dust mixed with half its weight of sulphur also burns freely, leaving white zinc sulphide.

The so-called *Lemery's volcano* was made by mixing iron filings with two-thirds of their weight of powdered sulphur, and burying several pounds of the moist mixture in the earth, when the heat evolved by the rusting of part of the iron provoked the energetic combination of the remainder with the sulphur, and the consequent development of much steam.* Firework compositions containing iron filings and sulphur may cause ignition if damp.

Several metals may be made to burn in sulphur vapour, as in oxygen, by heating the sulphur in a Florence flask, with a gauze burner, so as to keep the flask constantly filled with the brown vapour. Potassium and sodium, introduced in deflagrating spoons, take fire spontaneously in the vapour (fig. 192). A coil of copper wire glows vividly in sulphur vapour, and becomes converted into a brittle mass of sulphide of copper. When sulphur is exposed to sunshine in an atmosphere of hydride of antimony or arsenic, it becomes converted into hydrosulphuric acid gas and sulphide of antimony or arsenic.

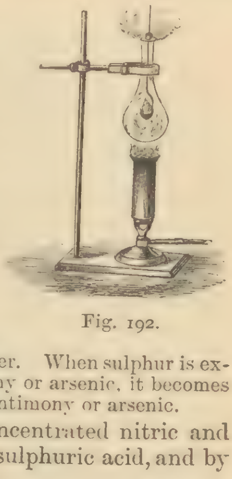

Fig. 192.

Sulphur dissolves, though slowly, in boiling concentrated nitric and sulphuric acids, being oxidised by the former into sulphuric acid, and by the latter into sulphur dioxide. It is far more rapidly converted into sulphuric acid by a mixture of nitric acid and potassium chlorate. The alkalies dissolve sulphur when heated, yielding yellow or red solutions which contain hyposulphites and sulphides of the alkali metals.

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* *Rust-joint cement* is a mixture of 80 parts iron filings, 1 of sal ammoniac, and 2 of sulphur, made into a paste with water; it is very useful for making the joints of iron tubes air-tight, for it sets into a hard cement, the iron combining with the sulphur.

There is a very general resemblance in composition between the compounds of sulphur and those of oxygen with the same elements.

139. *Influence of temperature upon the specific gravity of gases and vapours.*—The specific gravity of a gas or vapour being defined as its weight compared with that of an equal volume of dry and pure air at the same temperature and pressure, it might be supposed that so long as the temperatures were equal, their actual thermometric value would not influence the specific gravity. Indeed, with those gases and vapours which are condensible with difficulty, this is actually the case. Thus, if equal volumes of oxygen and air be weighed, either at a low or a high temperature, provided their temperatures are the same, their weights will always stand to each other nearly in the ratio of 1.1057 : 1.

But with many vapours it is found that if they be weighed at temperatures too nearly approaching to their condensing points, their specific gravities are much higher than they are found to be at higher temperatures. Sulphur affords a very well marked instance of this. It boils at 444° C., and if its vapour be weighed at a temperature of 480° C., it is found to weigh 6.617 times as much as an equal volume of air at 480° C., so that it is 96 times as heavy as hydrogen, or 1 atom of sulphur would occupy $\frac{1}{3}$ volume. But if the vapour of sulphur be weighed at 1000° C., it is found to weigh only 2.23 times as much as an equal volume of air at the same temperature and pressure, so that it is only 32 times as heavy as hydrogen, and 1 atom of sulphur occupies 1 volume.

According to Troost, the sulphur vapour at 480° C. is really a condensed molecule, like ozone, since its specific gravity remains unaltered under diminished pressure. Ozone $= O_3 = 2$ vols. Sulphur at 480° = $S_6 = 2$ vols.

HYDROSULPHURIC ACID, OR HYDRIC SULPHIDE.

$H_2S = 34$ parts by weight $= 2$ volumes.

140. *Sulphuretted hydrogen*, or *hydric sulphide*, or *hydrosulphuric acid*, has been already mentioned as occurring in some mineral waters, as at Harrogate. It is also found in the gases emanating from volcanoes, sometimes amounting to one-fourth of their volume. It is a product of the putrefaction of organic substances containing sulphur, and is one of the causes of the sickening smell of drains, &c. Eggs, which contain a considerable proportion of sulphur, evolve sulphuretted hydrogen as soon as they begin to change, and hence the association between this gas and the "smell of rotten eggs." The same smell is observed when a kettle boils over upon a coke or coal fire, the hydrogen liberated from the water combining with the sulphur present in the fuel.

Hydrosulphuric acid is also found among the products of destructive distillation of organic substances containing sulphur; it was mentioned among the products from coal, in which it is for the most part combined with the ammonia formed at the same time, producing ammonium sulphide.

It may be produced, though not in large quantity, by the direct union of hydrogen with sulphur vapour at a high temperature, or by passing a mixture of sulphur vapour and steam through a tube filled with red-hot pumice stone (the latter encouraging the action by its porosity). Hydrosulphuric acid is more readily formed by heating a damp mixture of sulphur and wood charcoal, and may be obtained in large quantity by heating a mixture of equal weights of sulphur and tallow or paraffin wax, the latter furnishing the hydrogen.

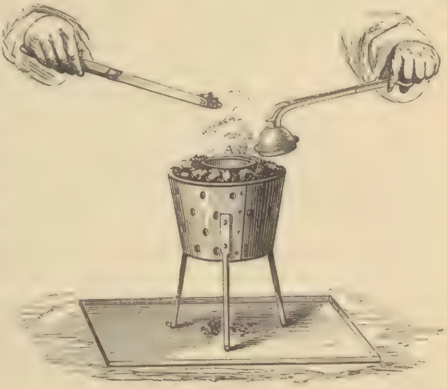

Fig. 193.

Preparation of hydrosulphuric acid.—For use in the laboratory, where it is very largely employed in testing for and separating metals, hydrosulphuric acid is generally prepared by decomposing ferrous sulphide with diluted sulphuric acid—

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

To obtain ferrous sulphide, a mixture of 3 parts of iron filings with 2 parts of flowers of sulphur is thrown, by small portions at a time, into an earthen crucible (A, fig. 193) heated to redness in a charcoal fire, the crucible being covered after each portion has been added. The iron and sulphur combine, with combustion, and when the whole of the mixture has been introduced, the crucible is allowed to cool, the mass of ferrous sulphide broken out, and a few fragments of it are introduced into a bottle (fig. 194) provided with a funnel tube for the addition of the acid, and a bent tube for conducting the gas through a small quantity of water, to remove any splashes of ferrous sulphate. From the second bottle the gas is conducted by a glass tube with a caoutchouc joint, either down into a gas-bottle, or into water, or any other liquid upon which the gas is intended to act. The fragments of ferrous sulphide should be covered with enough water to fill the gas-bottle to about one-third, and strong sulphuric acid added by degrees through the funnel, the bottle being shaken until effervescence is observed. An excess of strong sulphuric acid stops the evolution of gas by precipitating a quantity of white anhydrous ferrous sulphate, which coats the sulphide and defends it from the action of the acid. When no more gas is required, the acid liquid should be at once poured away, leaving the fragments of ferrous sulphide at the bottom of the bottle for a fresh operation. The liquid, if set aside, will deposit beautiful green crystals of *copperas* or ferrous sulphate ($FeSO_4.7H_2O$).

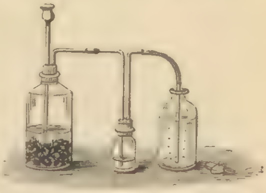

Fig. 194.—Preparation of hydrosulphuric acid.

Since the ferrous sulphide prepared as above generally contains a little metallic iron, the sulphuretted hydrogen is mixed with free hydrogen, which does not generally interfere with its uses. The pure gas may be prepared by heating antimony sulphide (crude antimony) in a flask with hydrochloric acid—

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

If hydrochloric acid be diluted with more than 6 molecules of water, it is not capable of decomposing the antimony sulphide; hence, when the sulphide is heated with an acid somewhat stronger than this, the subsequent addition of water reprecipitates the antimony sulphide with the orange colour which it always presents when precipitated.

Properties of hydrosulphuric acid.—This gas is at once distinguished from all others by its disgusting odour. It is one-fifth heavier than air (sp. gr. 1.1912). Its gaseous state is not permanent, but a pressure of 17 atmospheres is required to reduce it to a colourless liquid, which congeals to a transparent solid at – 122° F. Water absorbs about three times its volume of sulphuretted hydrogen at the ordinary temperature; both the gas and its solution are feebly acid to blue litmus-paper. The gas is very combustible, burning with a blue flame like that of sulphur, and yielding, as the chief products, water and sulphurous acid gas, $H_2S + O_3 = H_2O + SO_2$; a little sulphuric acid (H_2SO_4) is also formed, and unless the supply of air is very good, some of the sulphur will be separated; thus, if a taper be applied to a bottle filled with sulphuretted hydrogen, a good deal of sulphur will be deposited upon the sides. This combustibility of sulphuretted hydrogen is of the greatest importance in those processes of chemical manufacture in which this gas is evolved (as in the preparation of ammoniacal salts from gas liquors), enabling it to be disposed of in the furnace instead of becoming a nuisance to the neighbourhood. The gas causes fainting when inhaled in large quantity, and appears much to depress the vital energy when breathed for any length of time even in a diluted state.

When dissolved in water, hydrosulphuric acid is slowly acted upon by the oxygen of the air, which converts its hydrogen into water, and causes a white deposit of (electro-negative or soluble) sulphur.

This is a great drawback to the use of this indispensable chemical in the laboratory, since the solution of hydrosulphuric acid is so soon rendered useless. To obviate it as far as possible, the solution should be made either with boiled water (free from dissolved air), or with water which has already been once charged with the gas and spoilt by keeping, for all the oxygen dissolved in this water will have been consumed by the former portion of gas. The gas should be passed through the water until, on closing the bottle with the hand and shaking violently, the pressure is found to act outwards, showing the water to be saturated with the gas. By closing the bottle with a greased stopper, and inverting it, the solution may be preserved for some weeks, even though occasionally opened for use. The solution in glycerin keeps better, and is sold as a reagent.

In preparing the solution of hydrosulphuric acid, a certain quantity of the gas always escapes absorption. To prevent this from becoming a nuisance, the bottle containing the water to be charged with gas may be covered with an air-tight caoutchouc cap having two tubes, through one of which passes the glass tube conveying the gas down into the water, and through the other, a tube conducting the excess of gas either into a gas-burner, where it may be consumed, or into a solution of ammonia which will absorb it, forming the very useful ammonium sulphide.

A solution of magnesium hydrosulphide, $Mg(HS)_2$, is sold for preparing hydric sulphide by gently heating it.

Concentrated nitric acid acts upon hydric sulphide, oxidising the hydrogen and a part of the sulphur, ammonium sulphate being found in the solution, and a pasty mass of sulphur separated. Chlorine, bromine, and iodine at once appropriate its hydrogen and separate the sulphur.

Nitrous acid acts very readily upon hydric sulphide, yielding much ammonia; $HO.NO + 3H_2S = NH_3 + 2H_2O + S_3$.

In its action upon the metals and their oxides, hydrosulphuric acid resembles hydrochloric and the other hydrogen acids. Many of the metals displace the hydrogen and form metallic sulphides. This usually requires the assistance of heat, but mercury and silver act upon the gas at the ordinary temperature. Thus, if hydric sulphide be collected over mercury, the surface of the latter becomes coated with a black film of mercurous sulphide; $H_2S + Hg_2 = H_2 + Hg_2S$. In a similar way the surface of silver is slowly tarnished when exposed to air containing sulphuretted hydrogen, its surface being covered with a black film of silver sulphide. It is on this account that silver plate is so easily blackened by the air of towns. An egg spoon is always blackened by the sulphur from the egg. Silver coins kept in the pocket with lucifer matches are blackened, from the formation of a little silver sulphide. The original brightness of the coin may be restored by rubbing it with a solution of potassium cyanide, which dissolves the silver sulphide. Friction with strong ammonia will also remove the tarnish, and its application is safer than that of the poisonous cyanide.

When heated in the gas, several metals displace the hydrogen from it. Thus, potassium acts upon it in a corresponding manner to that in which it acts upon water, forming *potassium hydrosulphide* (KHS).

Tin removes the whole of the sulphur from hydrosulphuric acid at a moderate heat; $Sn + H_2S = H_2 + SnS$.

When hydrosulphuric acid acts upon a metallic oxide, it generally converts it into a sulphide corresponding to the oxide, whilst the hydrogen and oxygen unite to form water. Lead oxide in contact with the gas yields black lead sulphide and water; $PbO + H_2S = PbS + H_2O$. Paper impregnated with a salt of lead is used as a test for the presence of this gas. Thus, if paper be spotted with a solution of lead nitrate (or acetate) it will indicate the presence of even minute quantities of hydric sulphide (in impure coal gas, for example) by the brown colour imparted to the spots; $Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS$.

It is in this manner that paints containing white lead (lead carbonate) are darkened by exposure to the air of towns. Cards glazed with white lead, and engravings on paper whitened with that substance, suffer a similar change. Paintings, whether in oil or water-colours, in which lead is an ingredient, are also injured by air containing sulphuretted hydrogen. It has been found that such colours, damaged by the formation of lead sulphide, are restored by the continued action of light and air, the black sulphide becoming oxidised and converted into the white sulphate, $PbS + O_4 = PbSO_4$. In the dark this restoration does not take place, so that it is often a mistake to screen pictures from the light by a curtain.

The action of hydrosulphuric acid upon the chlorides and other haloid salts of the metals generally resembles its action upon the oxides of the same metals.

Most of the sulphides of the metals, like the corresponding oxides, are insoluble in water, but many of the sulphides are also insoluble in diluted acids and in alkalies, so that when hydrosulphuric acid is brought into contact with the solutions of metals, it will often precipitate the metal in the form of a sulphide having some characteristic colour or other property by which the metal may be identified.

Any solution of lead will give a *black* precipitate with solution of hydrosulphuric acid, the lead sulphide being insoluble in diluted acids and in alkalies.

A solution of antimony (tartar-emetic, for example, the tartrate of antimony and potassium), mixed with an excess of hydrochloric acid, gives an *orange*-coloured precipitate (Sb_2S_3) on adding hydrosulphuric acid; but if another portion be mixed with an excess of potash before adding the hydrosulphuric acid, there will be no precipitate, for the antimony sulphide is soluble in alkalies.

Cadmium chloride gives a brilliant *yellow* precipitate of cadmium sulphide on adding hydrosulphuric acid.

Zinc sulphate yields a *white* precipitate of zinc sulphide (ZnS), but if a little hydrochloric acid be previously added, no precipitate is formed, the zinc sulphide being soluble in acids. On neutralising the hydrochloric acid with ammonia, the zinc sulphide is at once precipitated.

It is evident that, in a solution containing cadmium and zinc, the metals may be separated by acidifying the liquid with hydrochloric acid, and adding excess of hydrosulphuric acid, which precipitates the cadmium sulphide only. On filtering the solution, and adding ammonia, the zinc sulphide is precipitated.

Sulphur-acids and *sulphur-bases.*—Those sulphides which are soluble in the alkalies are often designated sulphur-acids, whilst the sulphides of the alkali metals are sulphur-bases. These two classes of sulphides combine to form *sulphur-salts* analogous in composition to the oxygen-salts of the same metals. Thus, there have been crystallised, the salts—

Sodium sulphostannate	Na_4SnS_4
,, sulphantimoniate	$NaSbS_3$
,, sulpharseniate	Na_3AsS_4

The *action of air upon the sulphides* of the metals is often turned to account in chemical manufactures. At the ordinary temperature, the sulphides of those metals which form alkaline oxides (such as sodium and calcium), when exposed to the air in the presence of water, yield first, mixtures of the hydrate and bisulphide, $2Na_2S + O + H_2O = Na_2S_2 + 2NaHO$; and afterwards the hyposulphite, $Na_2S_2 + O_3 = Na_2S_2O_3$. This change is sometimes turned to account for the manufacture of sodium hyposulphite.

When the metal forms a less powerful base with oxygen, the sulphide is often converted into sulphate by exposure to moist air; thus, $CuS + O_4 = CuSO_4$, which is taken advantage of for the separation of copper from tin ores.

The black ferrous sulphide (FeS), when exposed to moist air, becomes converted into red ferric oxide, with separation of sulphur, $2FeS + O_3 = Fe_2O_3 + S_2$, a change which enables the gas manufacturer to revive, by the action of air, the ferric oxide employed for removing the sulphuretted hydrogen from coal gas.

When *roasted* in air at a high temperature, the sulphides corresponding to the more powerful bases are converted into sulphates; thus, $ZnS + O_4 = ZnSO_4$, which explains the production of zinc sulphate by roasting blende. But in most cases part of the sulphur is converted into sulphurous acid gas at the same time. Cuprous sulphide, for instance, is partly converted into cupric oxide by roasting, $Cu_2S + O_4 = 2CuO + SO_2$, a change of great importance in the extraction of copper from its ores.

141. *Hydric persulphide.*—The composition of this substance is not yet satisfactorily ascertained. The similarity of its chemical properties to those of hydric peroxide prompts the wish that its formula may be H_2S_2. Some analyses, however, seem to lead to the formula H_2S_5, but since the persulphide is a liquid capable of dissolving free sulphur, which is not easily separated from it, there is much difficulty in determining the exact proportion of this element with which the hydrogen is combined.

When equal weights of slaked lime and sulphur are boiled with water, an orange-coloured liquid is formed, which contains calcium hyposulphite, calcium disulphide, and calcium pentasulphide (CaS_5); $3CaO + S_6 = CaS_2O_3 + 2CaS_2$.

When hydrochloric acid is added to the filtered solution, an abundant precipitation of sulphur occurs, and much hydrosulphuric acid is evolved; $CaS_2 + 2HCl = CaCl_2 + H_2S + S$. But if the solution be poured by degrees into a slightly warm mixture of hydrochloric acid with twice its bulk of water, and constantly stirred, a yellow heavy oily liquid collects at the bottom, which is the hydric persulphide; $CaS_2 + 2HCl = H_2S_2\,(?) + CaCl_2$. The acid having been kept in excess, the persulphide has been preserved from the decomposition which it suffered in the presence of the alkaline solution in the former experiment. For the hydric persulphide very closely resembles the peroxide in the facility with which it may be decomposed into hydrosulphuric acid and sulphur; it undergoes spontaneous decomposition even in sealed tubes, and the hydrosulphuric acid then becomes liquefied by its own pressure. Most of the substances, the contact of which promotes the decomposition of the hydric peroxide, have the same effect upon the persulphide. This compound has a peculiar odour, which affects the eyes; of course, its vapour is mixed with that of hydrosulphuric acid resulting from its decomposition. Its specific gravity is 1.73.

OXIDES OF SULPHUR.

142. Only two important compounds of sulphur with oxygen have been obtained in the separate state, viz., *sulphurous anhydride* (SO_2) and *sulphuric anhydride* (SO_3). *Sulphur sesquioxide* (S_2O_3) and *persulphuric oxide* (S_2O_7) have also been obtained.

SULPHUR DIOXIDE, OR SULPHUROUS ANHYDRIDE.

$SO_2 = 64$ parts by weight $= 2$ volumes.

143. In nature, sulphurous acid gas is but rarely met with; it exists in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (containing sulphur), it is so easily oxidised and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere. Sulphurous acid gas has been already mentioned as the sole product of the combustion of sulphur in dry air and oxygen,* but it is generally prepared for chemical purposes from sulphuric acid, by heating it with metallic copper—

$$2H_2SO_4 \text{ (sulphuric acid)} + Cu = CuSO_4 \text{ (copper sulphate)} + 2H_2O + SO_2.$$

300 grains (or 20 grms.) of copper clippings are heated in a Florence flask with 4 oz. (measured) (or 110 c.c.) of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card (see fig. 169, p. 155). Some time will elapse before the gas is evolved; for sulphuric acid acts upon copper only at a high temperature; but when the evolution of gas fairly commences, it will proceed very rapidly, so that it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapour of sulphuric acid, which renders it turbid.

When the operation is finished, and the flask has been allowed to cool, it will be found to contain a grey crystalline powder at the bottom of a brown liquid. The latter is the excess of sulphuric acid employed, and retains very little copper, since cupric sulphate is insoluble in strong sulphuric acid. If the liquid be poured off, and the flask filled up with water, and set aside for some time, the crystalline powder will dissolve, forming a blue solution of sulphate of copper, yielding that salt in fine prismatic crystals by evaporation and cooling. The dark powder remaining undissolved after extracting the whole of the sulphate, consists chiefly of cuprous sulphide (Cu_2S), the production of which is interesting, as showing how far the de-oxidising effect of the copper may be carried in this experiment.

Sulphur dioxide is a very heavy (sp. gr. 2.25) colourless gas, characterised by its odour of burning brimstone. It condenses to a clear liquid at 0° F. (the temperature of a mixture of ice and salt) even at the ordinary pressure of the air, and has been frozen to a colourless crystalline solid at $-105°$ F.

The liquefaction of the gas is easily exhibited by passing it down to the bottom of a tube (A, fig. 195) closed at one end, and surrounded with a mixture of pounded ice with half its weight of salt. The tube should have been previously drawn out to a narrow neck at B, which may afterwards be sealed by the blowpipe, the lower part of the tube being still surrounded by the freezing mixture, since the liquid sulphur dioxide boils at -8° C. The tube need not be very strong, for at the ordinary temperature the vapour exerts a pressure of only 2.5 atmospheres. Liquid sulphur dioxide is a convenient agent for producing (by its rapid evaporation) the low temperature (-39° F.) required to effect the solidification of mercury. A small globule of this metal may readily be frozen by dropping some liquid sulphur dioxide upon it in a watch-glass placed in a strong draught of air. The tube containing the sulphur dioxide should be held in a woollen cloth or glove. The attractive experiment of freezing water in a red-hot crucible may also be made with the liquid. A platinum crucible being heated to redness, and some liquid sulphur dioxide poured into it, from a tube which has been cooled for half an hour in ice and salt, the liquid becomes surrounded with an atmosphere of sulphurous acid gas, which prevents its contact with the metal (assumes the *spheroidal* state), and its temperature is reduced by its own evaporation to so low a degree that a little water allowed to flow into it will at once become converted into opaque ice. Liquid SO_2 is employed in freezing machines. The temperature -220° F. (-140° C.) is obtained by the evaporation of a solution of solid CO_2 in liquid SO_2. This mixture was employed in liquefying oxygen, hydrogen, and nitrogen under very high pressure.

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* According to Berthelot, a notable quantity of SO_3 is produced at the same time.

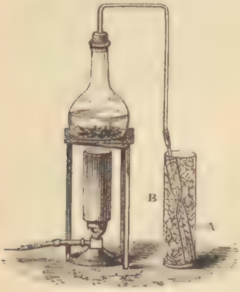

Fig. 195.

Sulphurous acid gas is very easily absorbed by water, as may be shown by pouring a little water into a bottle of the gas, closing the bottle with the palm of the hand, and shaking it violently (see fig. 161, p. 148), when the diminished pressure due to the absorption of the gas will cause the bottle to be sustained against the hand by the pressure of the atmosphere. Water absorbs 43.5 times its bulk of the gas at the ordinary temperature. The solution is believed to contain sulphurous acid, H_2SO_3, formed by the reaction $H_2O + SO_2 = H_2SO_3$, but this body has not been obtained in the separate state. If the solution be exposed to a low temperature, a crystallised hydrate is obtained, the composition of which does not appear to be accurately settled. When the solution of sulphurous acid is kept for some time in a bottle containing air, its smell gradually disappears, the acid absorbing oxygen and becoming converted into sulphuric acid.

Sulphur dioxide, like carbon dioxide, possesses in a high degree the power of extinguishing flame. A taper is at once extinguished in a bottle of the gas, even when containing a considerable proportion of air. One of the best methods of extinguishing burning soot in a chimney consists in passing up sulphurous acid gas by burning a few ounces of sulphur in a pan placed over the fire.

The principal uses of sulphurous acid gas depend upon its property of bleaching many animal and vegetable colouring matters. Although a far less powerful bleaching agent than chlorine, it is preferred for bleaching silk, straw, wool, sponge, isinglass, baskets, &c., which would be injured by the great chemical energy of chlorine. The articles to be bleached are moistened with water and suspended in a chamber in which sulphurous acid gas is produced by the combustion of sulphur. The colouring matters do not appear in general to be decomposed by the acid, but rather to form colourless combinations with it, for in course of time the original colour often reappears, as is seen in straw, flannel, &c., which become yellow from age, the sulphurous acid probably being oxidised into sulphuric acid. Stains of fruit and port wine on linen are conveniently removed by solution of sulphurous acid.

The red solution obtained by boiling a few chips of logwood with river water (distilled water does not give so fine a colour) serves to illustrate the bleaching properties of sulphurous acid. A few drops of the solution of the acid will at once change the red colour of the solution to a light yellow; but that the colouring power is suspended, and not destroyed, may be shown by dividing the yellow liquid into two parts, and adding to them, respectively, potash and diluted sulphuric acid, which will restore the colour in a modified form. To contrast this with the complete decomposition of the colouring matter, a little sulphurous acid may be added to a weak solution of the potassium permanganate, when the splendid red solution at once becomes perfectly colourless, and neither acid nor alkali can effect its restoration.

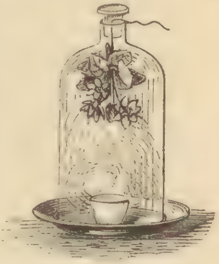
Fig. 196.

If a bunch of damp coloured flowers be suspended in a bell-jar over a crucible containing a little burning sulphur (fig. 196), many of the flowers will be completely bleached by the sulphurous acid; and by plunging them afterwards into diluted sulphuric acid and ammonia, their colours may be partly restored with some very curious modifications.

Another very useful property of sulphurous acid is that of arresting fermentation (or putrefaction), apparently by killing the vegetable or animal growth which is the cause of the fermentation. This is commonly designated the *antiseptic* or *antizymotic* property of sulphurous acid, and is turned to account when casks for wine or beer are *sulphured* in order to prevent the action of any substance contained in the pores of the wood, and capable of exciting fermentation, upon the fresh liquor to be introduced. If a little solution of sugar be fermented with yeast in a flask provided with a funnel tube (fig. 197), a solution of sulphurous acid poured in through the latter will at once arrest the fermentation. The salts of sulphurous acid (sulphites) are also occasionally used to arrest fermentation, in the manufacture of sugar, for instance. Clothes are sometimes fumigated with sulphurous acid gas to destroy vermin, and the air of rooms is disinfected by burning sulphur in it.

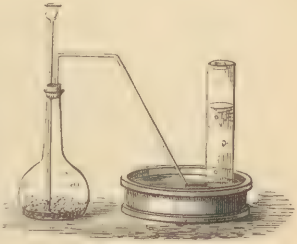
Fig. 197.

The disposition of sulphurous acid to absorb oxygen and pass into sulphuric acid, renders it a powerful de-oxidising or reducing agent. Solutions of silver and gold are reduced to the metallic state by sulphurous acid and sulphites.

If a solution of sulphurous acid be heated for some time in a sealed tube to 170° C., one portion of the acid de-oxidises another, sulphur is separated, and sulphuric acid formed; $3H_2SO_3 = 2H_2SO_4 + H_2O + S$.

Sulphurous acid gas combines with ammonia gas to form two solid compounds, $(NH_3)_2SO_2$ and $NH_3.SO_2$.

Chlorine combines with an equal volume of sulphur dioxide, under the influence of bright sunshine, or in presence of charcoal, to produce a colourless liquid, the vapour of which is very acrid and irritating to the eyes. Its composition is represented by SO_2Cl_2, and it is sometimes called *chlorosulphuric acid*, though it does not combine with bases, and is decomposed by water, yielding hydrochloric and sulphuric acids. It is also known as *sulphuryle chloride*. Its decomposition by water takes place in two stages: (1) $SO_2Cl_2 + H_2O = SO_2.Cl.HO + HCl$; (2) $SO_2.Cl.HO + H_2O = SO_2.HO.HO + HCl$; the final products being sulphuric and hydrochloric acids. The *chloride of thionyle*,* $SOCl_2$, is a colourless volatile liquid obtained by the action of sulphurous acid gas on phosphorus pentachloride. It is decomposed by water, yielding hydrochloric and sulphurous acids.

Potassium and sodium, when heated in sulphurous acid gas, burn vividly, producing the oxides and sulphides of the metals.

Iron, lead, tin, and zinc are also converted into oxides and sulphides when heated in sulphurous acid gas; $SO_2 + Zn_3 = ZnS + 2ZnO$.

Sulphites.—The acid character of sulphurous acid is rather feeble, although stronger than that of carbonic acid. There is much general resemblance between the sulphites and carbonates in point of solubility, the sulphites of the alkali metals being the only salts of sulphurous acid which are freely soluble in water. Sulphurous acid, H_2SO_3, being dibasic like carbonic, forms two classes of salts, the normal sulphites (for example, sodium sulphite, Na_2SO_3) and acid sulphites (as hydropotassium sulphite, $KHSO_3$).

Sodium sulphite is extensively manufactured for the use of the paper-maker, who employs it as an *antichlore* for *killing the bleach*, that is, neutralising the excess of chlorine after bleaching the rags with chloride of lime and sulphuric acid (see p. 161)—

$$Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl.$$

It is prepared by passing sulphurous acid gas over damp crystals of sodium carbonate, when carbonic acid gas is expelled, and sodium sulphite formed, which is dissolved in water and crystallised. It forms oblique prisms, having the composition $Na_2SO_3.7Aq$, which effloresce in the air, becoming opaque, and slowly absorbing oxygen, passing into sodium sulphate (Na_2SO_4). Its solution is slightly alkaline to test-papers.

For the manufacture of sodium sulphite the sulphurous acid gas is obtained either by the combustion of sulphur or by heating sulphuric acid with charcoal; $2H_2SO_4 + C = 2H_2O + CO_2 + 2SO_2$. The carbon dioxide of course will not interfere with this application of the sulphur dioxide.

SULPHURIC ACID, OR HYDRIC SULPHATE.

H_2SO_4 or $SO_2(OH)_2 = 98$ parts by weight.

144. More than four centuries ago, the alchemist Basil Valentine subjected *green vitriol*, as it was then called (sulphate of iron), to distillation, and obtained an acid liquid which he named *oil of vitriol*. The process discovered by this laborious monk is even now in use at Nordhausen in Saxony, and the *Nordhausen oil of vitriol* is an important article of commerce. The crystals of ferrous sulphate ($FeSO_4.7H_2O$) are exposed to the air so that they may absorb oxygen, and become converted into the *basic ferric sulphate*—

$$6FeSO_4 + O_3 = 2Fe_2(SO_4)_3.Fe_2O_3.$$

This salt is partially dried, and distilled in earthenware retorts, when a mixture of sulphuric acid and sulphuric anhydride distils over, and is sent into commerce as Nordhausen or *fuming sulphuric acid*: $Fe_2(SO_4)_3 + 2H_2O = Fe_2O_3 + 2H_2SO_4 + SO_3$. The ferric oxide ($Fe_2O_3$)

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* *Θεῖον, sulphur.*

which is left in the retorts, is the red powder known as *colcothar*, which is used for polishing plate glass and metals.

The green vitriol employed for preparing the Nordhausen acid is obtained from iron pyrites (FeS_2). A particular variety of this mineral, *white pyrites* (or efflorescent pyrites), when exposed to moist air, undergoes oxidation, yielding ferrous sulphate and sulphuric acid; $FeS_2 + H_2O + O_7 = FeSO_4 + H_2SO_4$.

Large masses of this variety of pyrites in mineralogical cabinets may often be seen broken up into small fragments, and covered with an acid efflorescence of ferrous sulphate from this cause. Ordinary iron pyrites is not oxidised by exposure to the air unless it be first subjected to distillation in order to separate a portion of the sulphur which it contains.

Fuming sulphuric acid (or *pyrosulphuric acid*) is now made in England by dissolving sulphuric anhydride in about twice its weight of oil of vitriol. In order to procure the sulphuric anhydride, oil of vitriol (H_2SO_4) is decomposed by a high temperature into steam, sulphurous acid gas, and oxygen; the vapour of water is removed by passing the gases through oil of vitriol, and the SO_2 and O are caused to combine by passing them over hot platinised asbestos. The fuming acid is kept in vessels of tinned iron, upon which it has no action.

The Nordhausen acid is readily distinguished from English sulphuric acid by its fuming in the air when the bottle is opened. This is due to the escape of a little vapour of sulphuric anhydride. It is heavier than the English acid, its specific gravity being 1.9. It is chiefly used for dissolving indigo in preparing the Saxony blue dye, also in making alizarine, and is a convenient source of the anhydride; for if it be gently heated in a retort, the anhydride is disengaged, and may be condensed in silky crystals in a receiver kept cool by ice, whilst ordinary sulphuric acid (H_2SO_4) is left in the retort.

An acid containing 40 or 50 per cent. of dissolved sulphuric anhydride is solid at ordinary temperatures, whilst that containing 60 or 70 per cent. is liquid even below 0° C.

The process adopted at Nordhausen, though simple in theory, is expensive, on account of the consumption of fuel and the breaking of the retorts, so that the price of the acid, compared with that of English manufacture, is very high.

The first step towards the discovery of our present process was also made by Valentine, when he prepared his *oleum sulphuris per campanum*, by burning sulphur under a bell-glass over water, and evaporating the acid liquid thus obtained. The same experimenter also made a very important advance when he burnt a mixture of sulphur, antimony sulphide, and nitre under a bell-glass placed over water; but it was not until the middle of the 18th century that it was suggested by some French chemists to burn the sulphur and nitre alone over water; a process by which the acid appears actually to have been manufactured upon a pretty large scale. The substitution of large chambers of lead for glass vessels by Dr. Roebuck was a great improvement in the process, and about the year 1770 the preparation of the acid formed an important branch of manufacture; since then the process has been steadily improving until, at the present time, upwards of 100,000 tons are annually consumed in Great Britain, and a very large quantity is exported. The diminution in the price of oil of vitriol well exhibits the progress of improvement in its production, for the original *oil of sulphur* appears to have been sold for about half-a-crown an ounce, and that prepared by burning sulphur with nitre in glass vessels at the same price per pound; but when leaden chambers were introduced, the price fell to a shilling per pound, and at present oil of vitriol can be purchased at the rate of five farthings per pound.

The description of the present process of manufacture will be best understood after a consideration of the chemical changes upon which it depends.

It has been seen that when sulphur is burnt in air, sulphur dioxide is the chief product. When this acts upon nitric acid, in the presence of water, sulphuric acid and nitrous anhydride are formed; $2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + N_2O_3$. The nitrous anhydride, in contact with air, steam, and SO_2, forms a crystalline compound—

$$N_2O_3 + O_2 + H_2O + 2SO_2 = 2(SO_2.OH.ONO),$$

crystals of the vitriol chambers. This crystalline compound is immediately decomposed by steam, with production of H_2SO_4—

$$2(SO_2.OH.ONO) + H_2O = N_2O_3 + 2(SO_2.OH.OH),$$

oil of vitriol. The N_2O_3 thus reproduced serves to convert more SO_2 into H_2SO_4 if the requisite quantities of air and steam be supplied.

It appears, therefore, that N_2O_3 may be employed to absorb oxygen from the air and to convey it to the SO_2, so that, theoretically, an unlimited quantity of sulphur might be converted into sulphuric acid by a given quantity of N_2O_3, with a sufficient supply of air and steam.

To illustrate the chemical principles of the manufacture of sulphuric acid, a large glass flask or globe (A, fig. 198) is fitted with a cork through which are passed (*a*) a tube connected with a flask (D) containing copper and strong sulphuric acid for evolving SO_2; (*b*) a tube connected with a flask (B) containing copper and diluted nitric acid (sp. gr. 1.2) for supplying nitric oxide; (*c*) a tube proceeding from a small flask (E) containing water.

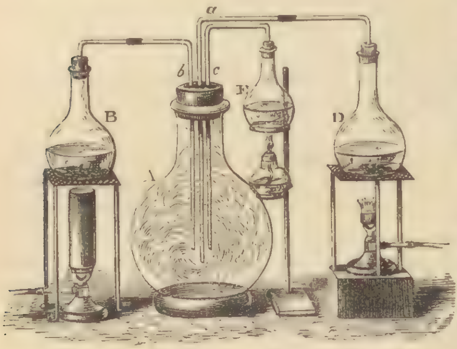

Fig. 198.—Preparation of sulphuric acid.

On heating the flask containing nitric acid and copper, the nitric oxide passes into the globe and combines with the oxygen of the air,* filling the globe with a red mixture of nitric peroxide and nitrous anhydride. The nitric oxide flask may then be removed. Sulphur dioxide is then generated by heating the flask containing sulphuric acid and copper; the sulphur dioxide will soon decolorise the red gas, the contents of the globe becoming colourless, and the crystalline compound forming abundantly on the sides; the sulphur dioxide flask may then be removed. Steam is sent into the globe from the flask containing water, when the crystalline compound will be dissolved, and sulphuric acid will collect at the bottom of the globe.

If the experiment be repeated, the steam being introduced simultaneously with the sulphur dioxide, no crystalline compound whatever will be formed, the sulphur dioxide being at once converted into sulphuric acid.

Since the cork is somewhat corroded in this experiment, it is preferable to have the mouth of the flask ground and closed by a ground glass plate, perforated with holes for the passage of the tubes. The perforations are easily made by placing the glass plate flat against the wall and piercing it with the point of a revolving rat's-tail file dipped in turpentine; the file is then gradually worked through the hole until the latter is of the required size.

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* The operation is, of course, more striking if oxygen is employed instead of air, the globe in fig. 198 being filled with oxygen by displacement at the commencement.

The process employed for the manufacture of English oil of vitriol will now be easily understood.

A series of chambers is constructed of leaden plates, the edges of which are united by autogenous soldering (that is, by fusing their edges, without solder, which would be rapidly corroded by the acid vapours); the leaden chambers are supported and strengthened by a framework of timber (fig. 199).

The *sulphurous acid gas* is generated by burning sulphur or iron pyrites in a suitable furnace (A) adjoining the chambers, and so arranged that the gas produced may be mixed with about the proper quantity of *air* to furnish the oxygen required for its conversion into sulphuric acid.

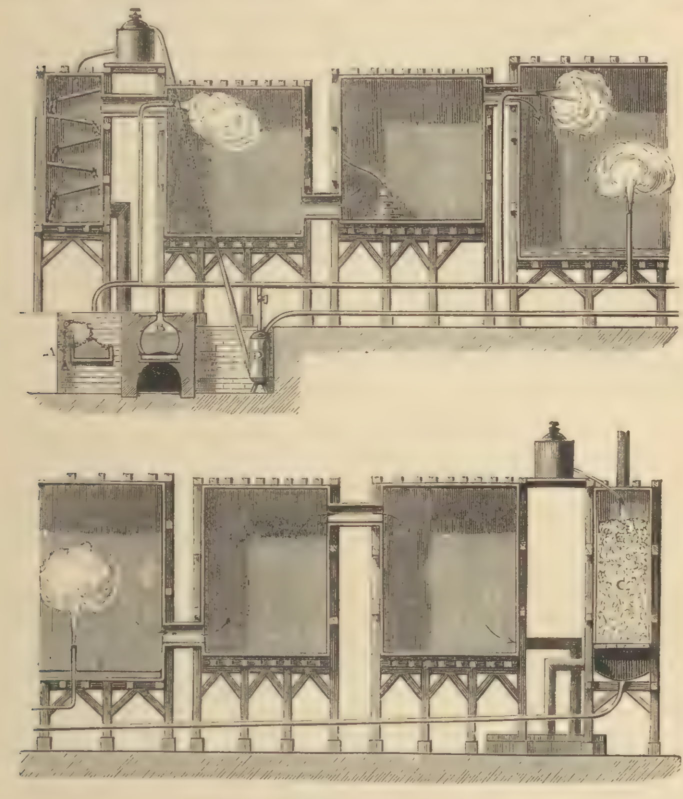

Fig. 199.—Sulphuric acid chambers.

Nitric acid vapour is evolved from a mixture of sodium nitrate and oil of vitriol (see p. 134) contained in an iron pan which is heated by the combustion of the sulphur, so that the nitric acid is carried into the chambers with the current of sulphurous acid gas and air.

Water covers the floor of the chambers to the depth of about 2 inches, and jets of steam are introduced at different parts from an adjacent boiler (B).

The sulphurous acid gas acts upon the nitric acid vapour, in the presence of the water, forming nitrous anhydride and sulphuric acid, which rains down into the water on the floor of the chambers. If the N_2O_3 were permitted to escape from the chambers, and a fresh quantity of nitric acid vapour introduced to oxidise another portion of sulphur dioxide, 2 molecules (170 parts by weight) of sodium nitrate would be required to furnish the nitric acid for the conversion of 2 atoms (64 parts by weight) of sulphur, whereas, in practice, 6 parts by weight only of nitrate are employed for 96 parts of sulphur.

The nitrogen of the air takes no part in the change; and since the oxygen consumed in converting the sulphur into sulphuric acid is accompanied by four times its volume of nitrogen, a very large accumulation of this gas takes place in the chambers, and provision must be made for its removal in order to allow space for those gases which take part in the change. The obvious plan would appear to be the erection of a simple chimney for the escape of the nitrogen at the opposite end of the chamber to that at which the sulphurous acid gas and air enter it: and this plan was formerly adopted, but the nitrogen carries off with it a portion of the nitrous anhydride which is so valuable in the chamber, and to save this the escaping nitrogen is now generally passed through a leaden chamber (Gay-Lussac's tower) (C) filled with coke, over which oil of vitriol is allowed to trickle: the oil of vitriol absorbs the N_2O_3, and flows into a cistern (D), from which it is forced up, by the pressure of steam, to the top of another chamber (Glover's tower) (E) arranged with shelves in cascade, through which the hot sulphurous acid gas and air are made to pass as they enter, when they take up the nitrous anhydride from the oil of vitriol, and carry it with them into the chamber.

Before the introduction of this plan, it required a quantity of sodium nitrate amounting to $\frac{1}{8}$th or $\frac{1}{10}$th of the weight of the sulphur to convert it into sulphuric acid, whereas about $\frac{1}{20}$th, or even less, is now often made to suffice.

In the vitriol chambers represented in fig. 199, the mixture of gases passing from the first square chamber into the second contains a large excess of sulphurous acid gas, which is oxidised and converted into sulphuric acid by the nitric acid flowing down the cascade represented at the entrance to the second chamber. The mixture of sulphuric acid with excess of nitric acid and other oxides of nitrogen which is thus formed, is made to pass back into the first chamber, in order to be de-oxidised by the excess of sulphurous acid gas. It is thence conducted by a pipe, not shown in the figure, into the middle chamber of much larger size, where the principal reaction between the sulphurous acid gas, the N_2O_3, and the oxygen of the air, takes place. The reaction is completed during the passage through the two last small chambers, and the gases are finally cooled by passing through a chamber surrounded with cold water before being discharged into the *Gay-Lussac's tower* (C).

The sulphuric acid is allowed to collect on the floor of the chamber until it has a specific gravity of about 1.6, and contains 70 per cent. of oil of vitriol (H_2SO_4). If it were allowed to become more concentrated than this, it would absorb some of the oxides of nitrogen in the chamber, so that it is now drawn off.

This acid is quite strong enough for some of the applications of sulphuric acid, particularly for that which consumes the largest quantity in this country, viz., the conversion of common salt into sodium sulphate as a preliminary step in the manufacture of carbonate of soda. To save the expense of transporting the acid for this purpose, the *vitriol chambers* form part of the plant of the alkali works.

To convert this weak acid into the ordinary oil of vitriol of commerce, it is run off into shallow leaden pans set in brickwork, and supported on iron bars over the flue of a furnace, where it is heated until so much water has evaporated that the specific gravity of the acid has increased to 1.72. The concentration cannot be carried further in leaden pans, because the strong acid acts upon the lead, and converts it into sulphate—

$$2H_2SO_4 + Pb = PbSO_4 + 2H_2O + SO_2.$$

The concentration of the acid is now often effected by high pressure steam passing through leaden worms immersed in the acid which is contained in wooden vats lined with lead.

The acid of 1.72 sp. gr. contains about 80 per cent. of true oil of vitriol, and is largely employed for making superphosphate of lime, and in other rough chemical manufactures. It is technically called *brown acid*, having acquired a brown colour from organic matter accidentally present in it.

To convert this brown acid into commercial oil of vitriol, it is boiled down, either in glass retorts or platinum stills, when water distils over, accompanied by a little sulphuric acid, and the acid in the retort becomes colourless, the brown carbonaceous matter being oxidised by the strong sulphuric acid, with formation of carbonic and sulphurous acid gases. When dense white fumes of oil of vitriol begin to pass over, showing that all the superfluous water has been expelled, the acid is drawn off by a siphon. The strongest acid obtainable by this process still contains about 2 per cent. of water, formed by the decomposition of some of the H_2SO_4 into H_2O and SO_3, which escapes as vapour.

The very diluted acid which distils off is employed instead of water on the floor of the leaden chamber.

The cost of the acid is very much increased by this concentration. It cannot be conducted in open vessels, partly on account of the loss of sulphuric acid, partly because concentrated sulphuric acid absorbs moisture from the open air even at the boiling point. The loss by breakage of the glass retorts is very considerable, although it is reduced as far as possible by heating them in sand, and keeping them always at about the same temperature by supplying them with hot acid. But the boiling point of the concentrated acid is very high (640° F.), and the retorts consequently become so hot that a current of cold air or an accidental splash of acid will frequently crack them at once. Moreover the acid boils with *succussion* or violent bumping, caused by sudden bursts of vapour, which endanger the safety of the retort.

With platinum stills the risk of fracture is avoided, and the distillation may be conducted more rapidly, the brown acid (sp. gr. 1.72) being admitted at the top, and the oil of vitriol (sp. gr. 1.84) drawn off by a platinum siphon from the bottom of the still, which is protected from the open fire by an iron jacket. But since a platinum still costs £2000 or £3000, the interest upon its value increases the cost of production of the acid.

When the perfectly pure acid is required, it is actually distilled over so as to leave the solid impurities (sulphate of lead, &c.) behind in the retort. Some fragments of rock crystal should be introduced into the retort to moderate the bursts of vapour, and heat applied by a ring gas-burner with somewhat divergent jets.

Properties of oil of vitriol.—The properties of concentrated sulphuric acid are very characteristic. Its great weight (sp. gr. 1.84),* freedom from odour, and oily appearance, distinguish it from any other liquid commonly met with, which is fortunate, because it is difficult to preserve a label upon the bottles of this powerfully corrosive acid. Although, if absolutely pure, it is perfectly colourless, the ordinary acid used in the laboratory has a peculiar grey colour, due to traces of organic matter. Its high boiling point, 338° C. (640° F.), has been already noticed; and although its vapour is perfectly transparent in the vessel in which the acid is boiled, as soon as it issues into the air it condenses into voluminous dense clouds of a most irritating description. Even a drop of the acid evaporated in an open dish will fill a large space with these clouds. Oil of vitriol solidifies when cooled to about −34° C (−30° F.), but the acid once solidified requires a temperature of 10°.5 C. (51° F.) to liquefy it again. Oil of vitriol rapidly corrodes the skin and other organic textures upon which it falls, usually charring or blackening them at the same time. Poured upon a piece of wood, the latter speedily assumes a dark brown colour; and if a few lumps of sugar be dissolved in a very little water, and stirred with oil of vitriol, a violent action takes place, and a semi-solid black mass is produced. This property of sulphuric acid is turned to account in the manufacture of blacking, in which treacle and oil of vitriol are employed. These effects are to be ascribed to the powerful attraction of oil of vitriol for water. Woody fibre ($C_6H_{10}O_5$) (which composes the bulk of wood, paper, and linen), and sugar ($C_{12}H_{22}O_{11}$), may be regarded, for the purpose of this explanation, as composed of carbon associated with 5 and 11 molecules of water, and any cause tending to remove the water would tend to eliminate the carbon.

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* The acid containing 97.7 per cent. has the highest sp. gr. 1.8413; that of 98 per cent., 1.8412; 99 per cent., 1.8403; 99.47 per cent., 1.8395; 100 per cent., 1.8384.

The great attraction of this acid for water is shown by the high temperature (often exceeding the boiling point of water) produced on mixing oil of vitriol with water, which renders it necessary to be careful in diluting the acid.

The water should be placed in a jug, and the oil of vitriol poured into it in a thin stream, a glass rod being used to mix the acid with the water as it flows in. Ordinary oil of vitriol becomes turbid when mixed with water, from the separation of lead sulphate (formed from the evaporating pans), which is soluble in the concentrated, but not in the diluted acid, so that if the latter be allowed to stand for a few hours, the lead sulphate settles to the bottom, and the clear acid may be poured off free from lead. Diluted sulphuric acid has a smaller bulk than is occupied by the acid and water before mixing.

The heat evolved on combining one molecular weight of H_2SO_4, with one of water amounts to 69.7 centigrade units. Decreasing quantities of heat are evolved for successive additions of water, until 120 molecules of water have been added.

Even when largely diluted, sulphuric acid corrodes textile fabrics very rapidly, and though the acid be too dilute to appear to injure them at first, it will be found that the water evaporates by degrees, leaving the acid in a more concentrated state, and the fibre is then perfectly rotten. The same result ensues at once on the application of heat; thus, if characters be written on paper with the diluted acid, they will remain invisible until the paper is held to the fire, when the acid will char the paper, and the writing will appear intensely black.

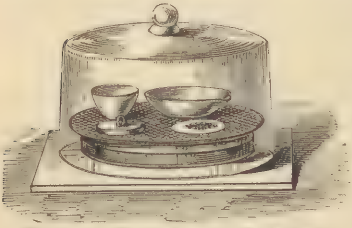

Fig. 200.—Drying over oil of vitriol.

If oil of vitriol be left exposed to the air in an open vessel, it very soon increases largely in bulk from the absorption of water, and a flat dish of oil of vitriol under a glass shade (fig. 200) is frequently employed in the laboratory for drying substances without the assistance of heat. The drying is of course much accelerated by placing the dish on the plate of an air-pump, and exhausting the air from the shade, so as to effect the drying *in vacuo*. It will be remembered also that oil of vitriol is in constant use for drying gases.

At a red heat, the vapour of oil of vitriol is decomposed into water, sulphur dioxide, and oxygen ; $H_2SO_4 = H_2O + SO_2 + O$.

When sulphur is boiled with oil of vitriol, the latter gradually dissolves the melted sulphur, converting it into sulphur dioxide—

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

All ordinary metals are acted upon by concentrated sulphuric acid when heated, except gold and platinum (the latter does not quite escape when long boiled with the acid), the metal being oxidised by one portion of the acid, which is thus converted into sulphur dioxide, the oxide reacting with another part of the sulphuric acid to form a sulphate. Thus, when silver is boiled with strong sulphuric acid, it is converted into silver sulphate, which is soluble in hot water—

$$Ag_2 + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$

Should the silver contain any gold, it is left behind in the form of a dark powder. Sulphuric acid is extensively employed for the separation or *parting* of silver and gold. This acid is also employed for extracting gold from copper ; and when sulphate of copper is manufactured by dissolving that metal in sulphuric acid (see p. 197), large quantities of gold are sometimes extracted from the accumulated residue left undissolved by the acid. If the sulphuric acid contains nitric acid, it dissolves a considerable quantity of gold, which separates again in the form of a purple powder when the acid is diluted with water, the sulphate of gold formed being reduced by the nitrous acid when the solution is diluted.

Some of the uses of sulphuric acid depend upon its specific action on certain organic substances, the nature of which has not yet been clearly explained. Of this kind is the conversion of paper into *vegetable parchment* by immersion in a cool mixture of two measures of oil of vitriol and one measure of water, and subsequent washing. The conversion is not attended by any change in the weight of the paper.

Sulphuric acid forms definite combinations with water. By evaporating diluted sulphuric acid *in vacuo* at 212° F., an acid is left which has the composition $H_2SO_4.2H_2O$ (sp. gr. 1.63). If this acid be evaporated in air at 400° F. (204° C.) as long as steam escapes, the remaining acid has the composition $H_2SO_4.H_2O$ (sp. gr. 1.78). This acid is called *glacial sulphuric acid*, because it solidifies to a mass of ice-like crystals at 47° F. (8° C.). It is sometimes sold instead of H_2SO_4, and may be known by its freezing in winter.

Proof of the composition of sulphuric acid.—10 grammes of sulphuric acid are neutralised by 22.7 grms. of PbO, when heated, giving off 1.82 grms. of H_2O and leaving 30.9 grms. of lead sulphate. Hence sulphuric acid contains 2.02 per cent. of H. 10 grms. galena, containing 8.66 Pb and 1.34 S, when converted into lead sulphate by nitric acid, yield 12.68 grms. Hence 12.68 grms. lead sulphate contain 1.34 S and 2.68 O, being the difference between the lead sulphate and the lead sulphide. The 30.9 grms. of lead sulphate furnished by 10 grms. of sulphuric acid would therefore contain 3.26 S and 6.52 O, so that 100 parts of sulphuric acid contain 2.02 H, 32.6 S, and 65.2 O, which numbers, divided by the atomic weights, give 2 atoms of H, 1 atom of S, and 4 atoms of O. The molecular weight of sulphuric acid cannot be deduced from the sp. gr. of its vapour because it is dissociated into H_2O and SO_3. But it yields with KHO two salts, one containing an atom of K and an atom of H, and the other containing two atoms of K. Hence these salts must be $KHSO_4$ and K_2SO_4, and the molecule of the acid must be H_2SO_4.

145. *Anhydrous sulphuric acid*, or *sulphuric anhydride*, or *sulphur trioxide* ($SO_3 = 80$).—Sulphurous acid and oxygen gases combine to form sulphuric anhydride when passed through a tube containing heated platinum or certain metallic oxides, such as those of iron and chromium, the action of which in promoting the combination is not thoroughly understood.

The combination may be shown by passing oxygen from the tube A (fig. 201), connected with a gas-holder, through a strong solution of sulphurous acid (B), so that it may take up a quantity of that gas; afterwards through a tube (C) containing pumice-stone soaked with oil of vitriol, to remove the water; and then through a bulb (D) containing platinised asbestos (see p. 142). The mixture of the gases issuing into the air is quite invisible, but when the bulb is gently heated, combination takes place, and dense white clouds are formed in the air, from the combination of the sulphuric anhydride (SO_3) produced, with the atmospheric moisture. The clouds are best shown by conducting them, through a bent tube attached to D, into a large flask. If the vapour of SO_3 be passed into a little oil of vitriol in a small stoppered bottle, the acid absorbs the SO_3, producing *fuming sulphuric acid* (p. 200), which solidifies to a crystalline mass when it has taken up about half its weight of SO_3.

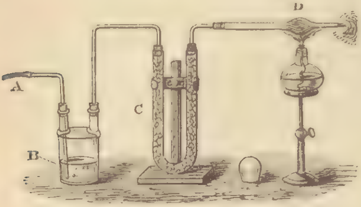

Fig. 201.

Pure sulphur trioxide, prepared by repeated distillation out of contact with moisture, is a mobile liquid which crystallises when cooled, in long transparent prisms like nitre, which fuse at 14°.8 C. and boil at 46° C. The commercial product, which has absorbed a little water, forms an opaque crystalline mass which fuses with great difficulty. When sulphuric acid in small quantity is added to this, it dissolves it, and on cooling to 8° C. crystals of $H_2SO_4.3SO_3$ are deposited. When more H_2SO_4 is added, it forms *pyrosulphuric acid*, $H_2SO_4.SO_3$ or $H_2S_2O_7$.

It has been stated that pure SO_3 is capable of alteration in its fusing point without any absorption of water.

When exposed to air, sulphur trioxide gives off strong white fumes caused by the combination of its vapour with the moisture of the air. It deliquesces in a short time, and becomes sulphuric acid—

$$SO_3 + H_2O = H_2SO_4.$$

When thrown into water, it hisses like red-hot iron, from the sudden formation of steam. The vapour is decomposed, as mentioned above, into sulphurous acid gas and oxygen, when passed through a red-hot tube. Phosphorus burns in its vapour, combining with the oxygen and liberating sulphur. Baryta glows when heated in the vapour of sulphuric anhydride, and combines with it to form barium sulphate.

Sulphuric anhydride is capable of combining with olefiant gas (C_2H_4) and similar hydrocarbons, and absorbs these from mixtures of gases. In the analysis of coal gas, a fragment of coke wetted with Nordhausen sulphuric acid is passed up into a measured volume of the gas standing over mercury to absorb these illuminating hydrocarbons. SO_3 also combines with HCl, forming $SO_2.Cl.HO$, which may also be obtained by distilling sulphuric acid with phosphoric chloride—

$$3SO_2(HO)_2 + PCl_5 = 3(SO_2.Cl.HO) + PO_2.HO + 2HCl.$$

An interesting method of obtaining the sulphuric anhydride consists in pouring 2 parts by weight of oil of vitriol over 3 parts of phosphoric anhydride, contained in a retort cooled in ice and salt, and afterwards distilling at a gentle heat, when the phosphoric anhydride retains water, and the SO_3 may be condensed in a cooled receiver.

When oil of vitriol is converted into vapour, its molecular weight (98 parts) is found to yield 4 volumes of vapour instead of 2, which is explained by a dissociation or temporary decomposition of the molecule of H_2SO_4 into H_2O (2 volumes) and SO_3 (2 volumes). On cooling, these recombine to form H_2SO_4.

146. *Sulphates—Action of sulphuric acid upon metallic oxides.*—At common temperatures sulphuric acid is capable of displacing all other acids from their salts; many cases will be remembered in which this power of sulphuric acid is turned to account.

So great is the acid energy of sulphuric acid, that when it is allowed to act upon an indifferent or acid metallic oxide, it causes the separation of a part of the oxygen, and reacts with the basic oxide so produced. Advantage is sometimes taken of this circumstance for the preparation of oxygen; for instance, when manganese dioxide is heated with sulphuric acid, sulphate of manganese is produced, and oxygen disengaged—

$$MnO_2 + H_2SO_4 = MnSO_4 + O + H_2O.$$

Again, if chromic anhydride be treated in the same way, chromic sulphate will be produced, with liberation of oxygen—

$$2CrO_3 + 3H_2SO_4 = Cr_2.3SO_4 + O_3 + 3H_2O.$$

A mixture of potassium dichromate ($K_2O.2CrO_3$) and sulphuric acid is sometimes used as a source of oxygen.

Sulphuric acid is a *dibasic* acid, that is, it contains two atoms of hydrogen which may be replaced by a metal. In *normal sulphates*, both atoms of H are so replaced, as in K_2SO_4, the normal potassium sulphate. When only a part of the H is replaced, *acid sulphates* are produced; thus $KHSO_4$ is acid potassium sulphate, which is very useful in blowpipe and metallurgic chemistry, because, when heated, it yields normal potassium sulphate and sulphuric acid; $2KHSO_4 = K_2SO_4 + H_2SO_4$. When the two atoms of H in H_2SO_4 are replaced by different metals, *double sulphates* are formed; potassium-alum, $KAl(SO_4)_2$, is an example of this class, in which one-fourth of the H in $2H_2SO_4$ is replaced by potassium, and the other three atoms by triatomic aluminium.

The following table exhibits the composition of the sulphates most frequently met with:—

Chemical Name.	Common Name.	Formula.
Potassium sulphate	Sal polychrest	K_2SO_4
Sodium sulphate	Glauber's salt	$Na_2SO_4.10H_2O$
Hydropotassium sulphate	Bisulphate of potash	$KHSO_4$
Ammonium sulphate		$(NH_4)_2SO_4$
Barium sulphate	Heavy spar	$BaSO_4$
Calcium sulphate	Gypsum	$CaSO_4.2H_2O$

COMPOSITION OF SULPHATES—(*continued*).

Chemical Name.	Common Name.	Formula.
Magnesium sulphate	Epsom salts	$MgSO_4.7H_2O$
Potassium-aluminium sulphate	Potash-alum	$KAl(SO_4)_2.12H_2O$
Ammonium-aluminium sulphate	Ammonia-alum	$NH_4Al(SO_4)_2.12H_2O$
Potassium-chromium sulphate	Chrome-alum	$KCr(SO_4)_2.12H_2O$
Ferrous sulphate	Green vitriol Copperas	$FeSO_4.7H_2O$
Manganous sulphate	. . . . . .	$MnSO_4.5H_2O$
Zinc sulphate	White vitriol	$ZnSO_4.7H_2O$
Lead sulphate	. . . . . .	$PbSO_4$
Cupric sulphate	Blue vitriol Blue stone	$CuSO_4.5H_2O$

In consequence of the tendency of sulphuric acid to break up into sulphur dioxide and oxygen at a high temperature, most of the sulphates are decomposed by heat; cupric sulphate, for example, when very strongly heated, leaves cupric oxide, whilst sulphur dioxide and oxygen escape; $CuSO_4 = CuO + SO_2 + O$. Ferrous sulphate is more easily decomposed; $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$.

The normal sulphates of potassium, sodium, barium, strontium, calcium, and lead are not decomposed by heat, and sulphate of magnesium is only partly decomposed at a very high temperature.

When a sulphate of an alkali or alkaline earth metal is heated with charcoal, the carbon removes the whole of the oxygen, and a sulphide of the metal remains, thus:—K_2SO_4 (*Potassium sulphate*) + C_4 = K_2S (*Potassium sulphide*) + $4CO$. Hydrogen, at a high temperature, effects a similar decomposition.

Even at the ordinary temperature, calcium sulphate in solution is sometimes de-oxidised by organic matter; this may occasionally be noticed in well and river waters when kept in closed vessels; they acquire a strong smell of hydric sulphide, in consequence of the conversion of a part of the calcium sulphate into sulphide by the organic constituents of the water, and the subsequent decomposition of the calcium sulphide by the carbonic acid present in the water.

Acids containing Hydrogen, Sulphur, and Oxygen.

Sulphurous	H_2SO_3
Sulphuric	H_2SO_4
Thiosulphuric (formerly hyposulphurous)	$H_2S_2O_3$
Dithionous	$H_2S_2O_4$
Dithionic	$H_2S_2O_6$
Trithionic	$H_2S_3O_6$
Tetrathionic	$H_2S_4O_6$
Pentathionic	$H_2S_5O_6$

147. *Hyposulphurous* or *thiosulphuric acid** ($H_2S_2O_3$).—This acid has not been obtained in the separate state; but many salts are known which are evidently derived from it, and such salts are called *hyposulphites* or *thiosulphates*.

The *sodium hyposulphite* is by far the most important of these salts, being very largely employed in photography, and as a substitute for sodium sulphite as an *antichlore.* The simplest method of preparing it consists in digesting powdered roll sulphur with solution of sodium sulphite (Na_2SO_3), when the latter dissolves an atom of sulphur and becomes hyposulphite ($Na_2S_2O_3$), which crystallises from the solution, when sufficiently evaporated, in fine prismatic crystals, having the formula $Na_2S_2O_3.5H_2O$.

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* Ὑπό, *under*, containing less oxygen than sulphurous acid. The name hyposulphurous acid is now often bestowed upon dithionous acid.

On a large scale, sodium hyposulphite is more economically prepared from the calcium hyposulphite obtained by exposing the refuse (*tank-waste* or *soda-waste*) of the alkali works to the air for some days. This refuse contains a large proportion of calcium sulphide, which becomes converted into hyposulphite by oxidation; $2CaS + O_4 = CaS_2O_3 + CaO$.

The hyposulphite is dissolved out by water, and the solution mixed with sodium carbonate, when calcium carbonate is precipitated and sodium hyposulphite remains in solution—

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

The most remarkable and useful property of the sodium hyposulphite is that of dissolving the chloride and iodide of silver, which are insoluble in water and most other liquids.

On mixing a solution of silver nitrate with one of sodium chloride, a white precipitate of silver chloride is obtained, the separation of which is promoted by stirring the liquid; $AgNO_3 + NaCl = AgCl + NaNO_3$. The precipitate may be allowed to settle and washed twice or thrice by decantation. One portion of the silver chloride is transferred to another glass, mixed with water, and solution of sodium hyposulphite added by degrees. The silver chloride is very easily dissolved, yielding an intensely sweet solution, which contains the hyposulphite of sodium and silver, produced by double decomposition between the silver chloride and sodium hyposulphite; $AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$. The sodium silver hyposulphite may be obtained in crystals from the solution.

When the silver chloride is acted on by a smaller proportion of the hyposulphite, another hyposulphite of sodium and silver is formed, which is very insoluble in water; $2AgCl + 3Na_2S_2O_3 = Ag_2Na_4(S_2O_3)_3 + 2NaCl$. Hence the necessity for using a strong solution of the hyposulphite in fixing photographic prints.

If the other portion of the silver chloride be exposed to the action of light, and especially of direct sunlight, it assumes by degrees a dark slate colour, from the formation of silver subchloride; $4AgCl + H_2O = 2Ag_2Cl + HCl + HClO$. By treating this darkened silver chloride with sodium hyposulphite, as before, the unaltered silver chloride will be entirely dissolved, but the subchloride will be decomposed into monochloride, which dissolves in the hyposulphite, and metallic silver, which is left in a very finely divided state as a black powder; $Ag_2Cl = AgCl + Ag$. The application of these facts in photography is well illustrated by the following experiments:—A sheet of paper is soaked for a minute or two in a solution of 10 grains of common salt in an ounce of water contained in a flat dish. It is then dried, and soaked for three minutes in a solution of 50 grains of silver nitrate in an ounce of water. The paper thus becomes impregnated with silver chloride formed by the decomposition between the sodium chloride and the silver nitrate. It is now hung up in a dark place to dry. If a piece of lace, or a fern leaf, or an engraving on thin paper, with well-marked contrast of light and shade, be laid upon a sheet of the prepared paper, pressed down upon it by a plate of glass and exposed for a short time to sunlight, a perfect representation of the object will be obtained, those parts of the sensitive paper to which the light had access having been darkened by the formation of silver subchloride, whilst those parts which were protected from the light remain unchanged.

But if this photographic print were again exposed to the action of light, it would soon be obliterated, the unaltered silver chloride in the white parts being acted on by light in its turn. The print is therefore *fixed* by soaking it for a short time in a saturated soluiton of sodium hyposulphite, which dissolves the white unaltered silver chloride entirely, and decomposes the subchloride formed by the action of light, leaving the black, finely divided metallic silver in the paper. The print should now be washed for two or three hours in a gentle stream of water, to remove all the silver hyposulphite, when it will be quite permanent.

The power of sodium hyposulphite to dissolve silver chloride has also been turned to account for extracting silver from its ores, in which it is occasionally present in the form of chloride.

The behaviour of solution of sodium thiosulphate with powerful acids explains the circumstance that the thiosulphuric acid has not been isolated, for if the solution be mixed with a little diluted sulphuric or hydrochloric acid, it remains clear for a few seconds, and then becomes suddenly turbid from the separation of sulphur, at the same time evolving a powerful odour of sulphur dioxide; $H_2S_2O_3 = H_2O + S + SO_2$. This disposition of the thiosulphuric acid to break up into sulphur dioxide and sulphur also explains the precipitation of metallic sulphides, which often takes place when sodium thiosulphate is added to the acid solutions of the metals. Thus, if an acid solution of antimonious chloride (obtained by boiling crude antimony ore (Sb_2S_3) with hydrochloric acid) be added to a boiling solution of sodium thiosulphate, the sulphur, separated from the thiosulphuric acid, combines with the antimony to form a fine orange-red precipitate of antimonious sulphide (Sb_2S_3), which is used in painting under the name of *antimony vermilion*. On the large scale, the solution of calcium hyposulphite obtained from the alkali waste is employed in the preparation of antimony vermilion, as being less expensive than the sodium-salt. Lead hyposulphite dissolved in sodium hyposulphite is used as a hair-dye, depositing the black lead sulphide.

When crystals of sodium hyposulphite are heated in the air, they first fuse in their water of crystallisation, then dry up to a white mass, which burns with a blue flame, leaving a residue of sodium sulphate. If heated out of contact with air, sodium pentasulphide will be left with the sodium sulphate; $4(Na_2S_2O_3 5H_2O) = 20H_2O + 3Na_2SO_4 + Na_2S_5$.

Some of the reactions of sodium thiosulphate become more intelligible when the salt is represented as sodium sulphate, $SO_2(NaO)_2$, in which an atom of sulphur has displaced an atom of oxygen, $SO_2.NaO.NaS$.

Dithionous or *hydrosulphurous acid* * ($H_2S_2O_4$).—When an aqueous solution of sulphurous acid is placed in contact with zinc, the metal is dissolved, forming a yellow solution without the usual evolution of hydrogen; the solution contains zinc dithionite; $2H_2SO_3 + Zn = ZnS_2O_4 + 2H_2O$.

The solution bleaches organic colours, even Prussian blue, and reduces the salts of silver, mercury, and copper to the metallic state. It is very unstable, soon becoming colourless zinc sulphite; $ZnS_2O_4 + O + H_2O = ZnSO_3 + H_2SO_3$.

The *sodium dithionite*, $Na_2S_2O_4$, is obtained by digesting zinc in solution of acid sulphite of sodium; $2NaHSO_3 + Zn = Na_2S_2O_4 + Zn(HO)_2$.

It forms needle-like crystals very soluble in water, insoluble in strong alcohol, and becoming acid sulphite of sodium, $NaHSO_3$, by absorption of oxygen from the air. By decomposing the sodium dithionite with oxalic acid, dithionous acid is obtained as an orange-yellow unstable liquid.

148. *Hyposulphuric acid*, or *dithionic acid* ($H_2S_2O_6$), has not at present acquired any practical importance. To prepare a solution of the acid, manganese dioxide in a state of fine division is suspended in water and exposed to a current of sulphur dioxide, the water being kept very cold whilst the gas is passing. A solution of manganous dithionate is thus obtained; $2SO_2 + MnO_2 = MnS_2O_6$. Some manganous sulphate is always formed at the same time; $SO_2 + MnO_2 = MnSO_4$, and if the temperature be allowed to rise, this will be produced in large quantity.

The solution containing the sulphate and dithionate is decomposed by solution of baryta (baryta-water), when manganous oxide is precipitated, together with barium sulphate, and barium dithionate is left in solution. To the filtered solution diluted sulphuric acid is carefully added until all the barium is precipitated as sulphate, when the solution of dithionic acid is filtered off and evaporated *in vacuo* over oil of vitriol. It forms a colourless inodorous liquid, which is decomposed, when heated, into sulphuric acid and sulphur dioxide; $H_2S_2O_6 = H_2SO_4 + SO_2$. Oxidising agents (nitric acid, chlorine, &c.) convert it into sulphuric acid.

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* Often called hyposulphurous acid.

The dithionates are not of any practical importance; they are all soluble, and are decomposed by heat, leaving sulphates, and evolving sulphur dioxide.

149. *Trithionic acid* ($H_2S_3O_6$) is also a practically unimportant acid. It is prepared from the potassium trithionate which is formed by boiling a strong solution of acid sulphite of potassium with sulphur until the solution becomes colourless, and filtering the hot solution from any undissolved sulphur; $6KHSO_3 + S = 2K_2S_3O_6 + K_2SO_3 + 3H_2O$. The solution deposits potassium trithionate in prismatic crystals. By dissolving these in water, and decomposing the solution with perchloric acid, the potassium is precipitated as perchlorate, and a solution of trithionic acid is produced, from which the acid has been obtained in crystals. It is, however, very unstable, being easily resolved into sulphur dioxide, sulphuric acid, and free sulphur; $H_2S_3O_6 = H_2SO_4 + SO_2 + S$.

150. *Tetrathionic acid* ($H_2S_4O_6$) is rather more stable than the preceding acid, though equally devoid of practical importance. It is formed when barium thiosulphate, suspended in a little water, is treated with iodine, when the tetrathionate is obtained in crystals; $2(BaS_2O_3) + I_2 = BaI_2 + BaS_4O_6$.

By exactly precipitating the barium from a solution of the tetrathionate by addition of diluted sulphuric acid, the solution of tetrathionic acid may be obtained. When the solution is boiled, it is decomposed into sulphuric acid, sulphur dioxide, and free sulphur; $H_2S_4O_6 = H_2SO_4 + SO_2 + S_2$.

When solution of ferric chloride is added to sodium thiosulphate, a fine purple colour is at first produced, which speedily vanishes, leaving a colourless solution. The purple colour appears to be due to the formation of the ferric thiosulphate, which speedily decomposes, the ultimate result being expressed by the equation $Fe_2Cl_6 + 2(Na_2S_2O_3) = Na_2S_4O_6 + 2FeCl_2 + 2NaCl$.

151. *Pentathionic acid* ($H_2S_5O_6$) possesses some interest as resulting from the action of hydric sulphide upon sulphurous acid, when much sulphur is deposited, and pentathionic acid remains in solution; $5H_2S + 5H_2SO_3 = H_2S_5O_6 + 9H_2O + S_5$. To obtain a concentrated solution of the acid, sulphuretted hydrogen and sulphur dioxide are passed alternately through the same portion of water until a large deposition of sulphur has taken place. This is allowed some hours to settle; the clear liquid poured off and the solution concentrated by evaporation, first over a water-bath, and finally, *in vacuo*, over oil of vitriol; for a concentrated solution of pentathionic acid is decomposed by heat into sulphuric acid and sulphur dioxide, with separation of sulphur; $H_2S_5O_6 = H_2SO_4 + SO_2 + S_3$.

Sulphur sesquioxide, S_2O_3, is an unstable blue crystalline solid, obtained by the gradual addition of sulphur to sulphuric oxide (SO_3) in the cold. It dissolves in fuming sulphuric acid to a blue liquid, but is decomposed by water, alcohol, or ether with separation of sulphur.

Persulphuric acid is the name given by Berthelot to a crystalline compound, S_2O_7 formed from SO_2 and O under the influence of electricity of high tension, or when hydric peroxide acts upon H_2SO_4. It is volatile and very unstable.

BISULPHIDE OF CARBON, OR CARBON DISULPHIDE.

$CS_2 = 76$ parts by weight.

152. This very important compound (also called *bisulphuret of carbon*) is found in small quantity among the products of destructive distillation of coal, and is very largely manufactured for use as a solvent for sulphur, phosphorus, caoutchouc, fatty matters, &c. It is one of the few compounds of carbon which can be obtained by the direct union of their elements, and is prepared by passing vapour of sulphur over charcoal heated to redness. It is remarkable that no heat is evolved in this act of combination.

In small quantity carbon disulphide is easily prepared in a tube of German glass (combustion-tube) about two feet long and half an inch in diameter, (fig. 202).

This tube is closed at one end, and a few fragments of sulphur dropped into it so as to occupy two or three inches. The rest of the tube is filled up with small fragments of recently calcined wood charcoal. The tube is placed in a combustion-furnace, and its open end connected by a perforated cork with a glass tube, which dips just below the surface of water contained in a bottle placed in a vessel of very cold water. That part of the tube which contains the charcoal is first surrounded with red-hot charcoal, and when it is heated to redness, a little red-hot charcoal is placed near the end containing the sulphur (hitherto protected by a sheet-iron screen), so that the vapour of sulphur may be slowly passed over the red-hot charcoal. The disulphide being insoluble in water, and much heavier (sp. gr. 1.27), is deposited beneath the water in the receiver. To purify the carbon disulphide from the water and the excess of sulphur which is deposited with it, the water is carefully drawn off with a small siphon, the disulphide transferred to a flask, and a few fragments of calcium chloride dropped into it to absorb the water. A bent tube connected with a Liebig's condenser, or with a worm, is attached to the flask (fig. 203) by a perforated cork, and the flask is gently heated in a water-bath, when the carbon disulphide is distilled over as a perfectly colourless liquid. The inflammability of the disulphide renders great care necessary.

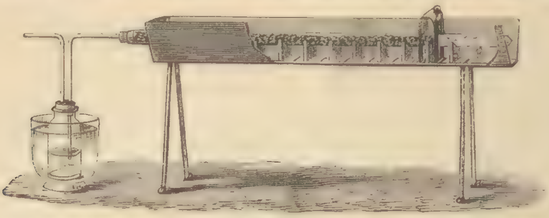
Fig. 202.

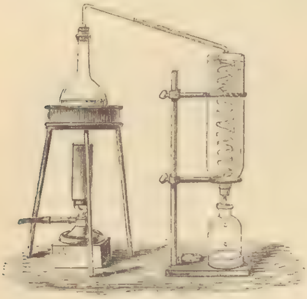
Fig. 203.

On a large scale, a fire-clay or cast-iron retort is filled with fragments of charcoal and heated to redness, pieces of sulphur being occasionally dropped in through an earthenware tube passing to the bottom of the retort. When very large quantities are made, coke is employed, and the vapour of sulphur is obtained from iron pyrites. The carbon disulphide is possessed of some very remarkable properties: it is a very brilliant liquid, the light passing through which at certain angles is partly decomposed into its component coloured rays before it reaches the eye. These properties are dependent upon its high refractive and dispersive powers, which are turned to great advantage in optical experiments, especially in *spectrum analysis*, where the rays emanating from a coloured flame are analysed by passing them through a prismatic bottle filled with carbon disulphide. It is also highly *diathermic*, that is, it allows rays of heat to pass through it with comparatively little loss, so that if it be rendered opaque to light by dissolving iodine in it, the rays of light emanating from a luminous object may be arrested, whilst the calorific rays are allowed to pass. Carbon disulphide is a very volatile liquid, readily assuming the form of vapour at the ordinary temperature, and boiling at 118°.5 F. (48° C.).

Its vapour, when diluted with air, has a very disgusting and exaggerated odour of sulphuretted hydrogen, but the smell at the mouth of the bottle is ethereal and not unpleasant if the disulphide has been carefully purified.

The rapid evaporation of carbon disulphide is, of course, productive of great cold. If a few drops be placed in a watch-glass and blown upon, they soon pass off in vapour, and the temperature of the glass is so reduced that some of the disulphide is frozen; this melts when the glass is placed in the palm of the hand. If a glass plate be covered with water, a watch-glass containing carbon disulphide placed on it, and evaporation promoted by blowing through a tube, the watch-glass will be frozen on to the plate, so that the latter may be lifted up by it.

The carbon disulphide is exceedingly inflammable; it takes fire at a temperature far below that required to inflame ordinary combustible bodies, and burns with a bright blue flame, producing carbonic and sulphurous acid gases ($CS_2 + O_6 = CO_2 + 2SO_2$), and having a great tendency to deposit sulphur unless the supply of air is very good.

The heat of combustion of CS_2 exceeds by 222 centigrade units the sum of the heat evolved by the combustion of its constituents in the separate form, this amount of heat having been absorbed in the act of combination between carbon and sulphur; hence carbon disulphide is endothermic.

If a little carbon disulphide be dropped into a small beaker, it may be inflamed by holding in its vapour a test-tube containing oil heated to about 300° F. (149° C.), which will be found incapable of firing gunpowder or of inflaming any ordinary combustible substance.

The abundance of sulphur separated in the flame of carbon disulphide enables it to burn iron by converting it into sulphide. If some carbon disulphide be boiled in a test-tube provided with a piece of glass tube from which the vapour may be burnt, and a piece of thin iron wire be held in the flame (fig. 204), it will burn with vivid scintillation, the fusible ferrous sulphide dropping off.

The vapour of carbon disulphide acts very injuriously if breathed for any length of time, producing symptoms somewhat resembling those caused by sulphuretted hydrogen. Its poisonous properties have been turned to account for killing insects in grain without injuring it.

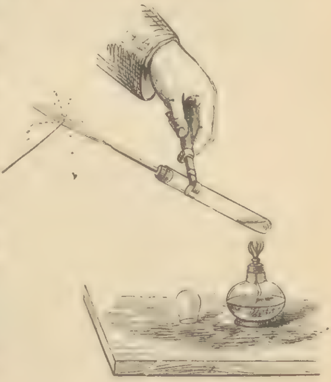

Fig. 204.

The chief applications of carbon disulphide depend upon its power of dissolving the oils and fats. After as much oil as possible has been extracted from seeds and fruits by pressure, a fresh quantity is obtained by treating the pressed cake with carbon disulphide, which is afterwards recovered by distillation from the oil. In Algiers it is employed for extracting the essential oils in which reside the perfumes of roses, jasmine, lavender, &c.

Carbon disulphide has often been made a starting-point in the attempts to produce organic compounds by synthesis. It may be employed in the formation of the hydrocarbons which are usually derived from organic sources; for if it be mixed with hydric sulphide (by passing that gas through a bottle containing the disulphide gently warmed), and passed over copper-turnings heated to redness in a porcelain tube, olefiant gas will be produced; $2CS_2 + 2H_2S + Cu_6 = 6CuS + C_2H_4$. Marsh gas may be obtained in the same way.

The action of carbon disulphide upon ammonia is practically important for the easy production of *ammonium sulphocyanide*, which is formed when the disulphide is dissolved in alcohol, and acted on by ammonia with the aid of heat; $CS_2 + 2NH_3 = H_2S + NH_4CNS$.

Carbon disulphide is often called sulphocarbonic acid; it combines with some of the sulphur-bases to form *sulphocarbonates* or *thiocarbonates*, which correspond to the carbonates, containing sulphur in place of oxygen. Thus when a solution of potassium sulphide is mixed with an excess of carbon disulphide, potassium sulphocarbonate is obtained in orange-yellow crystals. Even the hydrogen compound corresponding in composition to the unknown H_2CO_3 may be obtained as a yellow oily liquid by decomposing potassium sulphocarbonate with hydrochloric acid; $K_2CS_3 + 2HCl = H_2CS_3 + 2KCl$. Potassium thiocarbonate is applied for the destruction of the phylloxera insect which infests vines. As would be expected, the thiocarbonates, when boiled with water, exchange their sulphur for oxygen, becoming carbonates; $K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S$.

Small quantities of CS_2 may be identified by dissolving in alcoholic potash and adding cupric sulphate, which gives a yellow precipitate of ***cuprous xanthate***, $Cu_2S.CS.OC_2H_5$.

The carbon disulphide vapour in coal gas is one of the most injurious of the impurities, and one of the most difficult to remove with economy. It is especially injurious, because, when burning in the presence of aqueous vapour, a part of its sulphur is converted into sulphuric acid, the corrosive effects of which are so damaging. Several processes have been devised for its removal. Passing over-heated iron converts part of it into H_2S, which is removed in the purifiers. The gas has been washed with the *ammoniacal liquor* (containing ammonium sulphide), which absorbs the disulphide. Steam, at a high temperature, has been employed to convert it into hydrosulphuric acid and carbon dioxide, which are both easily removed from the gas; $CS_2 + 2H_2O = CO_2 + 2H_2S$. Lime at a red heat decomposes it in a similar way; $CS_2 + 3CaO = CaCO_3 + 2CaS$. Oxide of lead dissolved in caustic soda has been used to convert it into sulphide of lead; $CS_2 + 2PbO + 2NaHO = 2PbS + Na_2CO_3 + H_2O$. At present, however, it retains its character as one of the most troublesome impurities with which the gas manufacturer has to deal.

Carbon monosulphide, CS, is deposited when CS_2 is exposed to sunlight, or left for some weeks in contact with iron wire; $2CS_2 + Fe = FeS_2 + 2CS$. The FeS_2 is dissolved out by HCl, leaving the CS as a red-brown powder, of sp. gr. 1.66, insoluble in alcohol and benzene, slightly soluble in hot ether and CS_2. It is soluble in boiling nitric acid and in boiling strong potash. At about 200° C. it is decomposed into carbon, sulphur, and a little disulphide. It is converted into the latter by heating with excess of sulphur.

Carbon oxysulphide ($COS = 60$ parts by weight $= 2$ volumes).—This compound, which may be regarded as hydric sulphide in which CO has replaced H_2, is formed when a mixture of carbonic oxide with sulphur vapour is acted on by electric sparks, or passed through a red-hot porcelain tube.

It is easily prepared by gently heating the potassium sulphocyanide with oil of vitriol diluted with four-fifths of its volume of water, and collecting the gas over mercury. The action of the sulphuric acid upon the sulphocyanide produces hydrosulphocyanic acid; KCNS (potassium sulphocyanide) $+ H_2SO_4 = HCNS + KHSO_4$; which is then decomposed by the water in the presence of the excess of sulphuric acid, into the carbonic oxysulphide gas and ammonia, which combines with the sulphuric acid; $HCNS + H_2O = NH_3 + COS$. The gas has a peculiar disagreeable odour, recalling that of carbon disulphide; it is more than twice as heavy as air (sp. gr. 2.11), and is very inflammable, burning with a blue flame, and yielding carbonic and sulphurous acid gases. Potash absorbs and decomposes it, yielding carbonate and sulphide of potassium; $COS + 4KHO = K_2S + K_2CO_3 + 2H_2O$. Ammonia absorbs it freely, and, on evaporation, evolves H_2S and deposits crystals of urea; $COS + 2NH_3 = H_2S + CO(NH_2)_2$.

153. *Silicon disulphide* (SiS_2), corresponding in composition to carbon disulphide, is obtained by burning silicon in sulphur vapour, or by passing vapour of carbon disulphide over a mixture of silica and charcoal. Unlike the carbon compound, it is a white amorphous solid, absorbing moisture when exposed to air, and soluble in water, which gradually decomposes it into silica and hydric sulphide. When heated in air it burns slowly, yielding silica and sulphur dioxide.

154. *Nitrogen sulphide* (NS) is a yellow crystalline explosive substance, produced when chloride of sulphur, dissolved in carbon disulphide, is acted on by gaseous ammonia, $8NH_3 + 3S_2Cl_2 = 6NH_4Cl + 2NS + S_4$, when ammonium chloride is deposited, and the filtered liquid, allowed to evaporate, deposits sulphide of nitrogen mixed with sulphur, which may be dissolved out by carbon disulphide, in which the nitrogen compound is nearly insoluble; this substance is remarkable for its sparing solubility, its irritating odour, and its explosibility when struck or moderately heated, its elements being held together by a very feeble attraction.

Di-boron trisulphide (B_2S_3) is a yellowish, vitreous, volatile solid.

155. CHLORIDES OF SULPHUR.—The *subchloride*, or *chloride of sulphur*, or *sulphur monochloride* ($S_2Cl_2 = 135$ parts by weight), is the most important of these, since it is employed in the process of vulcanising caoutchouc. It is very easily prepared by passing dry chlorine over sulphur very gently heated in a retort (fig. 205); the sulphur quickly melts, and the sulphur monochloride distils over into the receiver as a yellow volatile liquid, boiling at 280° F. (138° C.), which has a most peculiar odour. It fumes strongly in air, the moisture decomposing it, forming hydrochloric and sulphurous acids, and causing a deposit of sulphur upon the neck of the bottle; $2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + S_3$.

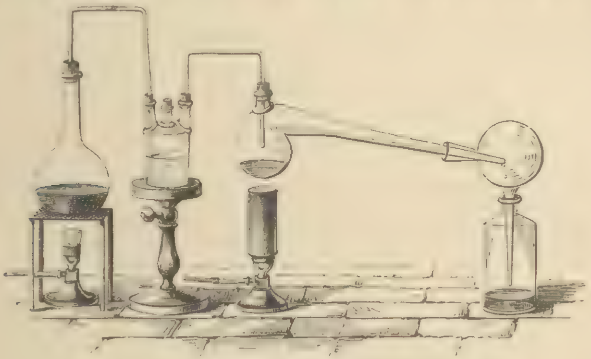

Fig. 205.—Preparation of sulphur monochloride.

When poured into water, it sinks (sp. gr. 1.68) and slowly undergoes decomposition; the separated sulphur, of course, belongs to the electro-positive variety (see p. 189), and the solution contains, beside hydrochloric and sulphurous acids, some of the acids containing a larger proportion of sulphur. If phosphorus dissolved in carbon disulphide be mixed with sulphur monochloride, the liquid will take fire on addition of ammonia. The specific gravity of the vapour of S_2Cl_2 is 4.7, showing that it is 68 times as heavy as hydrogen, giving for its molecular weight 136, which agrees very nearly with that calculated (135).

Sulphur dichloride (SCl_2) is a far less stable compound than the preceding chloride, from which it is obtained by the action of an excess of chlorine. It is a dark red fuming liquid, easily resolved, even by sunlight, into free chlorine and sulphur monochloride. *Sulphur tetrachloride* (SCl_4) has also been obtained.

Sulphur monobromide (S_2Br_2) is a liquid boiling at about 200° C.

Sulphur di-iodide (SI_2) is a crystalline unstable substance, produced by the direct union of its elements, and occasionally employed in veterinary medicine under the name of *black sulphur*.

Sulphur moniodide (S_2I_2) is obtained in large tabular crystals, resembling iodine, by decomposing the sulphur monochloride with ethyle iodide—

$$S_2Cl_2 + 2C_2H_5I = S_2I_2 + 2C_2H_5Cl.$$

Sulphur hexiodide (SI_6) is known.

SELENIUM.

Se = 79.5 parts by weight.

156. Selenium (Σελήνη, *the moon*) is a rare element, very closely allied to sulphur in its natural history, physical characters, and chemical relations to other bodies. It is found sparingly in the free state associated with some varieties of native sulphur, but more commonly in combination with metals, forming *selenides*, which are found together with the sulphides. The iron pyrites of Fahlun, in Sweden, is especially remarkable for the presence of selenium, and was the source whence this element was first obtained. The Fahlun pyrites is employed for the manufacture of oil of vitriol, and in the leaden chambers a reddish-brown deposit is found, which was analysed by Berzelius in 1817, and found to contain the new element.

In order to extract selenium from the seleniferous deposit of the vitriol works, it may be boiled with sulphuric acid diluted with an equal volume of water, and nitric acid added in small portions until the oxidation is completed, when no more red fumes will escape. The solution, containing selenious and selenic acids, is largely diluted with water, filtered from the undissolved matters, mixed with about one-fourth of its bulk of hydrochloric acid, and somewhat concentrated by evaporation, when the hydrochloric acid reduces the selenic to selenious acid—

$$H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2.$$

A current of sulphurous acid gas is now passed through the solution, when the selenium is precipitated in fine red flakes, which collect into a dense black mass when the liquid is gently heated; $H_2SeO_3 + H_2O + 2SO_2 = 2H_2SO_4 + Se$.

The proportion of selenium in the deposit from the leaden chambers is variable. The author has obtained 3 per cent. by this process.

Selenium, like sulphur, is capable of existing in three allotropic states: the red amorphous variety precipitated from its solutions, or sublimed like flowers of sulphur; the black vitreous form; and the crystalline form, deposited from its solution in carbon disulphide, in which it is far less easily dissolved than sulphur. Vitreous selenium, when heated, fuses at a little above 100° C., boils below a red heat, and is converted into a deep yellow vapour, which expands when heated in the same anomalous manner as vapour of sulphur. The crystalline selenium has a much higher fusing point.

Selenium is less combustible than sulphur; when heated in air it burns with a blue flame, and emits a peculiar odour like that of putrid horse-radish, which appears to be due to the formation of a little selenietted hydrogen from the moisture of the air. When heated with oil of vitriol, selenium forms a green solution which deposits the selenium again when poured into water.

Vitreous selenium is a very bad conductor of electricity, but crystalline selenium is a fair conductor, and conducts better in light than in darkness, which is taken advantage of in the *photophone*.

Selenium dioxide (SeO_2), corresponding to sulphur dioxide, is the product of combustion of selenium in oxygen. It is best obtained by dissolving selenium in boiling nitric acid (which would convert sulphur into sulphuric acid), and evaporating to dryness, when the selenium dioxide remains as a white solid which sublimes in needle-like crystals when heated. When dissolved in boiling water, it yields crystalline selenious acid, H_2SeO_3.

Selenic acid (H_2SeO_4).—Potassium selenate is formed when selenium is oxidised by fused nitre; $2KNO_3 + Se = K_2SeO_4 + 2NO$. By dissolving the potassium selenate in water, and adding lead nitrate, a precipitate of lead selenate ($PbSeO_4$) is obtained, and if this be suspended in water and decomposed by passing hydrosulphuric acid gas, lead will be removed as insoluble sulphide, and a solution of selenic acid will be obtained; $PbSeO_4 + H_2S = H_2SeO_4 + PbS$. This solution may be evaporated till it has a sp. gr. of 2.6, when it very closely resembles oil of vitriol. It is decomposed, however, at about 550° F., evolving oxygen, and becoming selenious acid. It oxidises the metals like oil of vitriol, and even dissolves gold. The selenates closely resemble the sulphates, but they are decomposed when heated with hydrochloric acid, chlorine being evolved and selenious acid produced.

Hydroselenic acid, or *seleniętted hydrogen* (H_2Se), is the analogue of sulphuretted hydrogen, and is produced by a similar process. It is even more offensive and poisonous than that gas, and acts in a similar way upon metallic solutions, precipitating the *selenides*.

There are two *chlorides of selenium:* the monochloride, Se_2Cl_2, a brown volatile liquid corresponding to sulphur monochloride; and the tetrachloride, $SeCl_4$, a white crystalline solid.

Notwithstanding the resemblance between the two elements, there are two *sulphides of selenium:* a disulphide (SeS_2) and a trisulphide (SeS_3). The former is obtained as a yellow precipitate when hydric sulphide acid is passed into solution of selenious acid.

TELLURIUM.

Te = 128 parts by weight.

157. Tellurium (from *tellus*, the earth) is connected with selenium by analogies stronger than those which connect that element with sulphur. It is even less frequently met with than selenium, being found chiefly in certain Transylvanian gold ores. It occasionally occurs in an uncombined form, but more frequently in combination with metals. It has recently been found in Colorado, masses of native tellurium up to 12 kilos. in weight having been met with; also *coloradoite*, or mercuric telluride, HgTe. Bismuth telluride, or *tetradymite*, Bi_2Te_3, has been found in California, and lead telluride, or *altaite*, in North Carolina. Foliated or *graphic tellurium*, or *sylvanite*, is a black material containing the tellurides of silver and gold. Arsenical pyrites sometimes contains tellurium, apparently as TeS_2.

Tellurium is extracted from the foliated ore by a process similar to that for obtaining selenium. From bismuth telluride it is procured by strongly heating the ore with a mixture of potassium carbonate and charcoal, when potassium telluride is formed, which dissolves in water to a purple-red solution, from which tellurium is deposited on exposure to air.

Tellurium much more nearly resembles the metals than the non-metals in its physical properties, and is on that account often classed among the former, but it is not capable of forming a true basic oxide. In appearance it is very similar to bismuth (with which it is so frequently found), having a pinkish metallic lustre, and being, like that metal, crystalline and brittle. It fuses below a red heat, and is converted into a yellow vapour at a high temperature. When heated in air it burns with a blue flame edged with green, and emits fumes of tellurium dioxide (TeO_2) and a peculiar odour.

Like selenium, tellurium is dissolved by strong sulphuric acid, yielding a purple-red solution, from which water precipitates it unchanged.

The *oxides of tellurium* correspond in composition to those of selenium. *Tellurous acid* (H_2TeO_3) is precipitated when a solution of tellurium in diluted nitric acid is poured into water. If the nitric solution is boiled, a crystalline precipitate of tellurous anhydride is obtained. Unlike selenious acid, tellurous acid is sparingly soluble in water. The anhydride is easily fusible, forming a yellow glass, which becomes white on cooling, and may be sublimed unchanged. Tellurous acid is rather a weak acid, and with some of the stronger acids the anhydride forms soluble compounds in which it takes the part of a very feeble base.

Telluric acid (H_2TeO_4) is also a weak acid obtained by oxidising tellurium with nitre, precipitating the potassium tellurate with barium chloride, and decomposing the barium tellurate with sulphuric acid. On evaporating the solution, crystals of telluric acid ($H_2TeO_4 2H_2O$) are obtained, which become H_2TeO_4 at a moderate heat, and when heated nearly to redness are converted into an orange-yellow powder, which is the anhydride. In this state it is insoluble in acids and alkalies. When strongly heated, it evolves oxygen, and becomes tellurous anhydride. The tellurates are unstable salts which are converted into tellurites when heated. Solutions of alkaline tellurates yield a precipitate of tellurium when boiled with alkaline carbonates and glucose.

Telluretted hydrogen, or *hydrotelluric acid* (H_2Te), exhibits in the strongest manner the chemical analogy of tellurium with selenium and sulphur. It is a gas very similar to sulphuretted hydrogen in smell, and in most of its other properties. When its aqueous solution is exposed to the air, it yields a brown deposit of tellurium. When passed into metallic solutions it precipitates the tellurides. The gas is prepared by decomposing telluride of zinc with hydrochloric acid.

The most characteristic property of tellurium compounds is that of furnishing the purple solution of potassium telluride, when fused with potassium carbonate and charcoal, and treated with water. Two solid *chlorides of tellurium* have been obtained: $TeCl_2$ is a black solid with a violet-coloured vapour, and is decomposed by water into tellurium and $TeCl_4$. The latter may be obtained as a white crystalline volatile solid, decomposed, by much water, into hydrochloric and tellurous acids. There are also two *sulphides of tellurium* corresponding to the oxides, from which they may be obtained as dark brown precipitates by the action of hydrosulphuric acid. They are both soluble in alkaline sulphides.

158. *Review of the sulphur group of elements.*—The three elements—sulphur, selenium, and tellurium—exhibit a relation of a similar character to that observed between the members of the chlorine group, both in their physical and chemical properties.

Sulphur is a pale yellow solid, easily fusible and volatile, without any trace of metallic lustre, and of specific gravity 2.05 (sp. gr. of vapour, 2.23). Selenium is either a red powder or a lustrous mass appearing black, but transmitting red light through thin layers; much less fusible and volatile than sulphur, and of specific gravity 4.8 (sp. gr. of vapour, 5.68). Tellurium has a brilliant metallic lustre, is much less fusible and volatile than selenium, and of specific gravity 6.65 (sp. gr. of vapour, 9.0).

Sulphur (atomic weight 32) has the most powerful attraction for oxygen, hydrogen, and the metals. Selenium (atomic weight 79.5) ranks next in the order of chemical energy. Tellurium (atomic weight 129) has a less powerful attraction for oxygen, hydrogen, and the metals, than either sulphur or selenium. This element appears to stand on neutral ground between the non-metallic bodies and the less electropositive metals.

PHOSPHORUS.

$P = 31$ parts by weight.*

159. This is the only element for the ordinary preparation of which animal substances are employed. It is never known to occur uncombined in nature, but it is found abundantly in the form of *phosphate of lime* or *tricalcic diphosphate*, $3CaO.P_2O_5$ or $Ca_3(PO_4)_2$, which is contained in the minerals *coprolite*, *phosphorite*, and *apatite*, and occurs diffused, though generally in small proportion, through all soils upon which plants will grow, for this substance is an essential constituent of the food of most plants, and especially of the cereal plants which form so large a proportion of the food of animals. The seeds of such plants are especially rich in the phosphates of calcium and magnesium.

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* The vapour of phosphorus is 62 times as heavy as hydrogen, so that its atom only occupies half a volume, if the atom of hydrogen be taken to occupy one volume: and the molecule of phosphorus (P_4) occupying two volumes, would consist of four atoms instead of two. At very high temperatures the specific gravity of phosphorus vapour diminishes, showing a tendency to conform to the ordinary law of volumes.

Animals feeding upon these plants still further accumulate the phosphorus, for it enters, chiefly in the form of calcium phosphate, into the composition of almost every solid and liquid in the animal body, and is especially abundant in the bones, which contain about three-fifths of their weight of calcium phosphate.

Composition of the Bones of Oxen.

Animal matter (*Osséine*)	30.58
Calcium phosphate	57.67
,, fluoride	2.69
,, carbonate	6.99
Magnesium phosphate	2.07
	100.00

What is here termed animal matter is a cartilaginous substance, converted into gelatin when the bones are heated with water under pressure, and containing carbon, hydrogen, nitrogen, and oxygen. It was formerly the custom to get rid of this by burning the bones in an open fire, but the increased demand for chemical products, and the diminished supply of bones, have taught economy, so that the cartilaginous matter is now dissolved out by heating the bones with water at a high pressure for the manufacture of glue; or the bones are subjected to destructive distillation, so as to save the ammonia which they evolve, and the bone charcoal thus produced is used by the sugar-refiner until its decolorising powers are exhausted, when it is heated in contact with air to burn away the charcoal, and leave the *bone-ash*, consisting chiefly of calcium phosphate, $Ca_3(PO_4)_2$. In order to extract the phosphorus, the bone-ash is heated for some time with diluted sulphuric acid, which removes the greater part of the calcium in the form of the sparingly soluble sulphate, leaving the phosphoric acid in the solution, which is strained from the deposit,

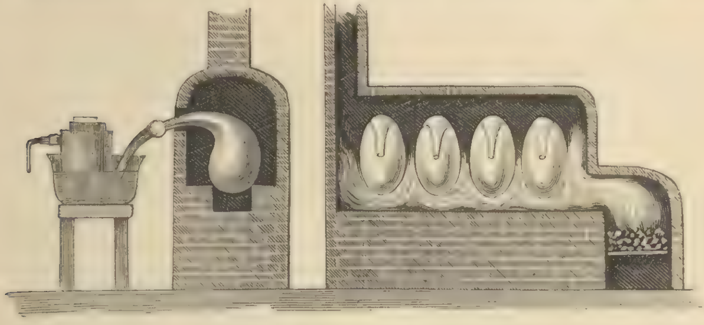

Fig. 206.—Extraction of phosphorus.

evaporated to a syrup, mixed with charcoal, thoroughly dried in an iron pot, and distilled in an earthen retort (fig. 206), when the carbon removes the oxygen, and phosphorus distils over, being condensed in a receiver containing water to protect it from the action of the air.

In this process, the sulphuric acid does not remove the whole of the calcium from the phosphate, a portion remaining in the solution containing the phosphoric acid, so that this solution is generally said to contain *superphosphate of lime*, and the action of the sulphuric acid is thus represented—

Bone phosphate, $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2$ (*superphosphate*) $+ 2CaSO_4$.

When the superphosphate is dried, it becomes converted into *calcium metaphosphate*, $Ca(PO_3)_2$; $CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O$, and on distilling this with charcoal; $3Ca(PO_3)_2 + C_{10} = Ca_3(PO_4)_2 + 10CO + P_4$.

On the small scale, for the sake of illustration, phosphorus may be prepared by a process which has also been successfully employed for its manufacture in quantity, and consists in heating a mixture of bone-ash and charcoal in a stream of hydrochloric acid gas; $Ca_3(PO_4)_2 + 6HCl + C_8 = 3CaCl_2 + 8CO + H_6 + P_2$.

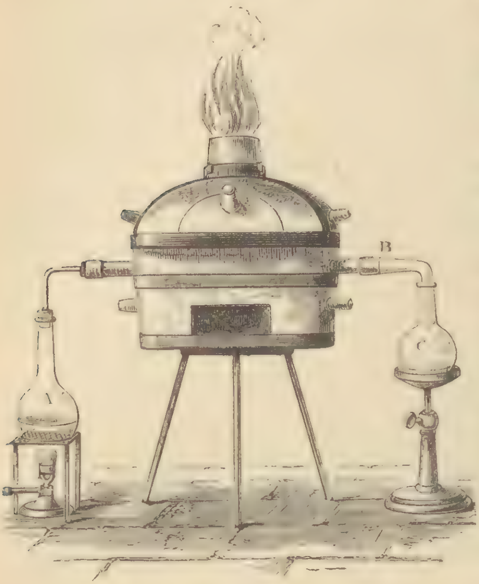

Fig. 207.

A mixture of equal weights of well-dried charcoal and bone-ash, both in fine powder, is introduced into a porcelain tube, and placed in a charcoal furnace (fig. 207). One end of the tube is connected with a flask (A), containing fused salt and sulphuric acid for evolving hydrochloric acid, and the other is cemented with putty into a bent retort neck (B), for conveying the phosphorus into a vessel of water (C). On heating the porcelain tube to bright redness, phosphorus distils over in abundance. The hydrogen and carbonic oxide inflame as they escape into the air, from their containing phosphorus vapour.

When first prepared, the phosphorus is red and opaque, from the presence of some suboxide of phosphorus and mechanical impurities; the latter are removed by melting the phosphorus under warm water, and squeezing it through wash-leather. The phosphorus is then fused under ammonia to remove any acid impurity, and afterwards under potassium dichromate acidified with sulphuric acid, when the chromic acid oxidises the suboxide of phosphorus, and converts it into phosphoric acid which dissolves. The phosphorus is then thoroughly washed, melted under water, and drawn up into glass tubes, or run into cylindrical copper moulds, where it solidifies into the sticks in which it is sold. These are always preserved under water from the action of oxygen and in tin cases from that of light.

Pure ordinary, or *vitreous*, phosphorus is almost colourless and transparent, but when exposed to light, and especially to direct sunlight, it gradually acquires an opaque red colour, from its partial conversion into the allotropic variety known as red or *amorphous phosphorus*. By tying bands of black cloth round a stick of phosphorus and exposing it, under water, to the action of sunlight, alternate zones of red may be produced.

Even though the phosphorus be screened from light, it will not remain unchanged unless the water be kept quite free from air, which irregularly corrodes the surface of the phosphorus, rendering it white and opaque. This action is accelerated by exposure to light.

The most remarkable character of ordinary phosphorus is its easy inflammability. It inevitably takes fire in air when heated a little above its melting point, 44° C. (111°.5 F.), burning with a brilliant white flame, which becomes insupportable when the combustion takes place in oxygen (p. 27), and evolving dense white clouds of phosphoric anhydride. When a piece of dry phosphorus is exposed to the air, it combines slowly with oxygen,* and its temperature often becomes so much elevated during this slow combustion, that it melts and takes fire, especially if the combustion be encouraged by the warmth of the hand or by friction. Hence, ordinary phosphorus must never be handled or cut in the dry state, but always under water, for it causes most painful burns.

The slow oxidation of phosphorus is attended with that peculiar luminous appearance which is termed *phosphorescence* (φῶς, *light*, φέρω, *to bear*), but this glow is not seen in pure oxygen or in air containing a minute proportion of olefiant gas or oil of turpentine. It will be remembered that the slow oxidation of phosphorus in moist air is attended with the formation of ozone.

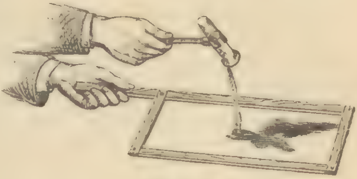
Fig. 208.

The characteristic behaviour of phosphorus in air is best observed when the phosphorus is in a finely divided state. When a fragment of phosphorus is shaken with a little carbon disulphide, it is quickly dissolved, and if the solution be poured upon a piece of filtering paper (fig. 208), and allowed to evaporate in a darkened room, the very thin film of phosphorus which is left will exhibit a glow increasing in brilliancy till the phosphorus bursts out into spontaneous combustion.

If phosphorus be dissolved in olive oil, at a gentle heat, the solution is strongly phosphorescent when shaken in a bottle containing air, or when rubbed upon the hands.

Characters may be written on paper with a stick of phosphorus held in a thickly folded piece of damp paper (having a vessel of water at hand into which to plunge the phosphorus if it should take fire). When the paper is held with its back to the fire, or to a hot iron, in a darkened room, a twinkling combustion of the finely divided phosphorus will ensue, and the letters will be burnt into the paper. Phosphorus which has been partly oxidised is even more easily inflamed than pure phosphorus. If a few small pieces of phosphorus be placed in a dry stoppered bottle, gently warmed till they melt, and then shaken round the sides of the bottle so as to become partly converted into red oxide of phosphorus, it will be found, long after the bottle is cold, to be spontaneously inflammable, so that if a wooden match tipped with sulphur be rubbed against it, the phosphorus which it takes up will ignite when the match is brought into the air, kindling the sulphur, which will inflame the wood. This was one of the earliest forms in which phosphorus was employed for the purpose of procuring an instantaneous light. If the stopper be greased, the phosphorus may be preserved unchanged for a long time.

In the last experiment, if the wood had not been tipped with sulphur, the phosphorus would not have kindled it, the flame of phosphorus generally being unable to ignite solid combustibles, because it deposits upon them a coating of P_2O_5, which protects them from the action of air. Hence, in the manufacture of lucifer matches, the wood is first tipped with sulphur, or wax, or paraffin, which easily give off combustible vapours to be kindled by the flame of the phosphorus composition, and thus to inflame the wood.

If a small stick of phosphorus be carefully dried with filtering paper, and dropped into a cylinder of oxygen, which is afterwards covered with a glass plate, no luminosity will be observed in a darkened room until the cylinder is placed under the air-pump receiver, and the air slowly exhausted. When the oxygen has thus been rarefied to about one-fifth of its former density, the phosphorescence will be seen. A similar effect may be produced by covering the cylinder of oxygen containing the phosphorus (having removed the glass plate) with another cylinder, about four times its size (fig. 209), filled with carbonic acid gas, which will gradually dilute the oxygen and produce phosphorescence. By suspending—in a bottle of air containing a strongly luminous piece of phosphorus—a piece of paper with a drop of oil of turpentine upon it, the glow may be almost instantaneously destroyed. A small tube of olefiant gas or coal gas dropped into the bottle will also extinguish the luminosity.*

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* The white fumes evolved by phosphorus in moist air are said to consist partly of ammonium nitrate, formed by the action of the ozonised oxygen upon the air and aqueous vapour.

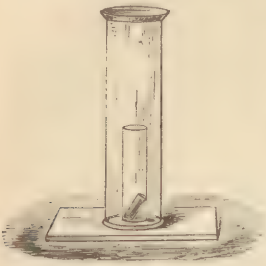

Fig. 209.

Ordinary phosphorus is slowly converted into vapour at common temperatures, and emits, in the air, white fumes with a peculiar alliaceous smell, which appear phosphorescent in the dark. When heated out of contact with air, it boils at 532° F. (278° C.), and is converted into a colourless vapour.

The luminosity of phosphorus vapour is seen to advantage when a piece of phosphorus is boiled with water in a narrow-necked flask or retort, or a test-tube with a cork and narrow tube. The steam charged with vapour of phosphorus has all the appearance of a blue flame, in a darkened room, but of course combustibles are not inflamed by it, since its temperature is not higher than 212° F. Phosphorus may be distilled, with perfect safety, in an atmosphere of carbonic acid gas, the neck of the retort being allowed to dip under water in the receiver.

Although ordinary phosphorus is of a decidedly glassy or *vitreous* structure, and not at all crystalline, it may be obtained in dodecahedral crystals, by allowing its solution in carbon disulphide to evaporate in an atmosphere of carbonic acid gas, or by fusing it in a tube exhausted by a Sprengel pump, and letting it cool in the dark.

The conversion of ordinary phosphorus into the red or *amorphous phosphorus* is one of the most striking instances of allotropic modification. When phosphorus is heated for a considerable length of time to about 450° F. (232° C.) *in vacuo*, or in an atmosphere in which it cannot burn, it becomes converted into a red infusible mass of amorphous phosphorus. This form of phosphorus differs as widely from the vitreous form as graphite differs from diamond. It is almost unchangeable in the air, evolves no vapour, is not luminous, cannot be inflamed by friction, or even by any heat short of 500° F. (260° C.), when it actually becomes reconverted into ordinary phosphorus.† By heating vitreous phosphorus in an exhausted and sealed tube to about 500° C., it is converted into a violet-black fused mass with cavities containing crystals. Amorphous phosphorus is insoluble in the solvents for ordinary phosphorus. The two varieties also differ greatly in specific gravity, that of the ordinary phosphorus being 1.83, and of the amorphous variety 2.14.

The conversion of vitreous into amorphous phosphorus may be effected by heating it in a flask (A, fig. 210) placed in an oil-bath (B), maintained at a temperature ranging from 450° to 460° F. (232° to 238° C.), the flask being furnished with a bent tube (C) dipping into mercury, and with another tube (D) for supplying carbonic acid gas, dried by passing over calcium chloride. The flask should be thoroughly filled with carbonic acid gas before applying heat, and the tube delivering it may then be closed with a small clamp (E). After exposure to heat for about forty hours, but little ordinary phosphorus will remain, and this may be removed by allowing the mass to remain in contact with carbon disulphide for some hours, and subsequently washing it with fresh disulphide till the latter leaves no phosphorus when evaporated.

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* Chappuis finds that when phosphorus is suspended in oxygen, the space glows for a short time on adding a little ozone.

† According to Hittorf, the reconversion does not take place till 800° F., the red phosphorus being convertible into vapour below that temperature, without fusion.

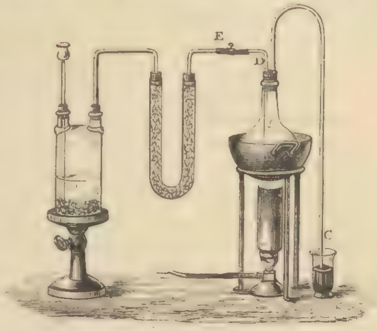

Fig. 210.

On the large scale, the red phosphorus is prepared by heating about 200 lbs. of vitreous phosphorus to 450° F. in an iron boiler. After three or four weeks the phosphorus is found to be converted into a hard red brittle mass, which is ground by millstones under water, and separated from the ordinary phosphorus either by carbon disulphide or caustic soda, in which the latter is soluble. The temperature requires careful regulation, for if it be allowed to rise to 500°, the red phosphorus quickly resumes the vitreous condition, evolving the heat which it had absorbed during its conversion, and thus converting much of the phosphorus into vapour. The heat evolved in the passage of the amorphous into the vitreous form amounts to 20,000 gramme-units for 31 grms. of phosphorus. This reconversion may be shown by heating a little red phosphorus in a narrow test-tube, when drops of vitreous phosphorus condense on the cool part of the tube. The colour of different specimens of amorphous phosphorus varies considerably; that prepared on the large scale is usually of a dark purplish colour, but it may be obtained of a bright scarlet colour. Rhombohedral crystals of phosphorus, resembling crystals of arsenic in form and metallic appearance, have been obtained by fusing phosphorus with lead, and dissolving out the latter with diluted nitric acid (sp. gr. 1.1). Similar crystals have been obtained by heating red phosphorus to 530° C. in a vacuous tube.

Ordinary phosphorus is very poisonous, whilst amorphous phosphorus appears to be harmless. The former is employed, mixed with fatty substances, for poisoning rats and beetles. Cases are, unhappily, not very rare, of children being poisoned by sucking the phosphorus composition on lucifer matches. The vapour of phosphorus also produces a very injurious effect upon the persons engaged in the manufacture of lucifer matches, resulting in the decay of the lower jaw-bone. The evil is much mitigated by good ventilation, or by diffusing turpentine vapour through the air of the workroom, and attempts have been made to obviate it entirely by substituting amorphous phosphorus for the ordinary variety, but, as might be expected, the matches thus made are not so sensitive to friction as those in which the vitreous phosphorus is used.

The difference between the two varieties of phosphorus, in respect to chemical energy, is seen when they are placed in contact with a little iodine on a plate, when the ordinary phosphorus undergoes combustion and the red phosphorus remains unaltered.

Ordinary phosphorus is capable of direct union with oxygen, chlorine, bromine, iodine, sulphur, and most of the metals, with which it forms *phosphides* or *phosphurets*. Even gold and platinum unite with this element when heated, so that crucibles of these metals are liable to corrosion when heated in contact with a phosphate in the presence of a reducing agent, such as carbon. Thus the inside of a platinum dish or crucible is roughened when vegetable or animal substances containing phosphates are incinerated in it. The presence of small quantities of phosphorus in metallic iron or copper produces considerable effect upon their physical qualities.

Phosphorus has the property, a very remarkable one in a non-metal, of precipitating some metals from their solutions in the metallic state. If a stick of phosphorus be placed in a solution of sulphate of copper, it becomes coated with metallic copper, the phosphorus appropriating the oxygen. This has been turned to advantage in copying very delicate objects by the electrotype process, for by exposing them to the action of a solution of phosphorus in ether or carbon disulphide, and afterwards to that of a solution of copper, they acquire the requisite conducting metallic film, even on their finest filaments. Solutions of silver and gold are reduced in a similar manner by phosphorus.

By floating very minute scales of ordinary phosphorus upon a dilute solution of chloride of gold, the metal will be reduced in the form of an extremely thin film, which may be raised upon a glass plate, and will be found to have various shades of green and violet by transmitted light, dependent upon its thickness, whilst its thickest part exhibits the ordinary colour of the metal to reflected light. By heating the films on the plate, various shades of amethyst and ruby are developed. If a very dilute solution of chloride of gold in distilled water be placed in a perfectly clean bottle, and a few drops of ether, in which phosphorus has been dissolved, poured into it, a beautiful ruby-coloured liquid is obtained, the colour of which is due to metallic gold in an extremely finely divided state, and on allowing it to stand for some months, the metal subsides as a purple powder, leaving the liquid colourless. If any saline impurity be present in the gold solution, the colour of the reduced gold will be amethyst or blue. These experiments (Faraday) illustrate very strikingly the use of gold for imparting ruby and purple tints to glass and the glaze of porcelain.

160. *Lucifer matches* are made by tipping the wood with sulphur, or wax, or paraffin, to convey the flame, and afterwards with the match composition, which is generally composed of saltpetre or potassium chlorate, phosphorus, red lead, and glue, and depends for its action on the easy inflammation, by friction, of phosphorus when mixed with oxidising agents like saltpetre (KNO_3), potassium chlorate ($KClO_3$), or red lead (Pb_3O_4), the glue only serving to bind the composition together and attach it to the wood. The composition used by different makers varies much in the nature and proportions of the ingredients. In this country, potassium chlorate is most commonly employed as the oxidising agent, such matches usually kindling with a slight detonation; but the German manufacturers prefer either potassium nitrate or lead nitrate, together with lead dioxide or red lead, which produce *silent matches.*

Sulphide of antimony (which is inflamed by friction with potassium chlorate, see p. 164) is also used in those compositions in which a part of the phosphorus is employed in the amorphous form, and fine sand or powdered glass is very commonly added to increase the susceptibility of the mixture to inflammation by friction.

The match composition is coloured either with ultramarine blue, Prussian blue, or vermilion. In preparing the composition, the glue and the nitre or chlorate are dissolved in hot water, the phosphorus then added and carefully stirred in until intimately mixed, the whole being kept at a temperature of about 100° F. The fine sand and colouring matter are then added, and when the mixture is complete, it is spread out upon a stone slab heated by steam, and the sulphured ends of the matches are dipped into it.

The *safety matches*, which refuse to ignite unless rubbed upon the sides of the box, are tipped with a mixture of antimony sulphide, potassium chlorate, and powdered glass, which is not sufficiently sensitive to be ignited by any ordinary friction, but inflames at once when rubbed upon the amorphous phosphorus mixed with glass, which coats the rubber on the sides of the box. On this principle some French matches have been made which can be ignited only by breaking the match and rubbing the two ends together.

It would be very desirable to dispense entirely with the use of phosphorus in lucifer matches, not only because of the danger from accident and disease in the manufacture, but because a very large quantity of phosphate of lime which ought to be employed for agricultural purposes is now devoted to the preparation of phosphorus, of which six tons are said to be consumed annually in this country for the manufacture of matches. The most successful attempt in this direction appears to be the employment of a mixture of potassium chlorate and lead hyposulphite, in place of the ordinary phosphorus composition.

For illustration, very excellent matches may be made upon the small scale in the following manner. The slips of wood are dipped in melted sulphur so as to acquire a slight coating. Thirty grains of gelatin or isinglass are dissolved in 2 drachms of water in a porcelain dish placed upon a steam-bath; 20 grains of ordinary phosphorus are then added, and well mixed in with a piece of wood; to this mixture are added, in succession, 15 grains of red lead and 50 grains of powdered potassium chlorate. The sulphured matches are dipped into this paste, and left to dry in the air.

To make the safety matches: 10 grains of powdered potassium chlorate and 10 grains of antimony sulphide are made into a paste with a few drops of a warm solution of 20 grains of gelatin in 2 drachms of water, the sulphured matches being tipped with this composition. The rubber is prepared with 20 grains of amorphous phosphorus, and 10 grains of finely powdered glass, mixed with the solution of gelatin, and painted on paper or cardboard with a brush.

161. *Phosphorus-fuze composition.*—To ignite the Armstrong percussion shells, a very sensitive detonating composition was employed, which is composed of amorphous phosphorus, potassium chlorate, shellac, and powdered glass, made into a paste with spirit of wine. This was placed in the little cap designed for it, and when dry, waterproofed with a little shellac dissolved in spirit. The fuzes were found too sensitive to bear transport.

Such a composition may be prepared *with care* in the following manner:—Four grains of powdered potassium chlorate are moistened on a plate with 6 drops of spirit of wine, 4 grains of powdered amorphous phosphorus are added, and the whole mixed, at arm's length, with a bone-knife, avoiding great pressure. The mixture, which should still be quite moist, is spread in small portions upon ten or twelve pieces of filtering paper, and left in a safe place to dry. If one of these be gently pressed with a stick, it explodes with great violence. It is dangerous to press it with the blade of a knife, as the latter is commonly broken, and the pieces projected with considerable force. A stick dipped in oil of vitriol of course explodes it immediately. If a bullet be placed very lightly upon one of the pellets, and the paper tenderly wrapped round it, a percussion shell may be extemporised, which explodes with a loud report when dropped upon the floor.

The detonating toys known as *amorces fulminantes* are made by enclosing this composition between two pieces of thin paper. 1000 of them contain 70 grains of the composition.

162. OXIDES OF PHOSPHORUS.—Four compounds of phosphorus and oxygen are known, their formulæ being P_4O, P_2O_3, P_2O_4, and P_2O_5.

Phosphoric Acids and Phosphates.

163. The phosphates are by far the most important of the compounds of phosphorus. They have been already noticed as almost the only forms of combination in which that element is met with in nature, and as indispensable ingredients in the food of plants and animals. No other mineral substance can bear comparison with calcium phosphate as a measure of the capability of a country to support animal life. Phosphoric acid itself is very useful in calico-printing and in some other arts.

The mineral sources of this acid appear to be *phosphorite*, *coprolite*, and *apatite*, all consisting essentially of calcium phosphate, $Ca_3(PO_4)_2$, but associated in each case with calcium fluoride, which is also contained, with calcium phosphate, in bones, and would appear to indicate an organic origin for these minerals. Phosphorite is an earthy-looking substance, forming large deposits in Estremadura. Apatite (from *ἀπατάω*, *to cheat*, in allusion to mistakes in its early analysis) occurs in prismatic crystals, and is met with in the Cornish tin-veins. Both these minerals are largely imported from Spain, Norway, and America. for use in this country as a manure. Coprolites (*κόπρος*, *dung*, *λίθος*, *a stone*, from the idea that they were petrified dung) are rounded nodules of calcium phosphate, which are found abundantly in this country.

Large quantities of phosphates of calcium and magnesium are imported in the form of *guano*, the partially decomposed excrement of sea-fowl.

Phosphoric acid is obtained from bone-ash by decomposing it with sulphuric acid, so as to remove as much of the lime as possible in the form of sulphate, which is strained off, and the acid liquid neutralised with ammonium carbonate, which precipitates any unchanged calcium phosphate, and converts the phosphoric acid into ammonium phosphate. On evaporating the solution, and heating the ammonium phosphate, ammonia and water are expelled, and metaphosphoric acid (HPO_3) is left in a fused state, solidifying to a glass on cooling. Thus prepared, however, it always retains some ammonia, and is contaminated with soda derived from the bones.

The pure acid is prepared by oxidising phosphorus with diluted nitric acid (sp. gr. 1.197) and evaporating the solution until the phosphoric acid begins to volatilise in white fumes; $5HNO_3 + P_3 = 3HPO_3 + H_2O + 5NO$. Some phosphorous acid is formed at an intermediate stage. A transparent glass (*glacial phosphoric acid*) is thus obtained, which eagerly absorbs moisture from the air, and becomes liquid. That which is sold in sticks contains much sodium metaphosphate.

The addition of a little bromine greatly facilitates the action of nitric acid upon phosphorus, apparently by forming the phosphorus pentabromide, which is then decomposed by water; $PBr_5 + 4H_2O = H_3PO_4 + 5HBr$. The hydrobromic acid being then acted on by nitric acid, bromine is set free to act upon a fresh quantity of phosphorus; $3HBr + HNO_3 = Br_3 + 2H_2O + NO$. When iodine is also added, the action is still better.

1 oz. (or 28 grms.) of phosphorus is placed in 6 oz. (or 170 c.c.) of water and 5 grs. (or 0.32 grm.) of iodine are added; then, drop by drop, 30 grs. (or 1.94 grms.) of bromine. When the action is over, 6 oz. (or 170 c.c.) of nitric acid (sp. gr. 1.42) are added, and the vessel is placed in cold water. When the phosphorus has dissolved, the solution is evaporated till its temperature rises to about 400° F. (204° C.) in order to expel the excess of nitric acid, the bromine, and the iodine.

Phosphoric anhydride, or *phosphorus pentoxide* (P_2O_5), is prepared by burning phosphorus in dry air.

When required in considerable quantity, the anhydride is prepared by burning the phosphorus in a small porcelain dish (A, fig. 211) attached to a wide glass tube (B) for introducing the phosphorus, and suspended in a glass flask with two lateral necks, one of which is connected with a tube containing pumice-stone and oil of vitriol for drying the air as it enters, whilst the other neck is provided with a wide tube conveying the anhydride into a bottle, connected, at C, with an aspirator, or cistern of water, for drawing air through the apparatus. The first piece of phosphorus is kindled by passing a hot wire down the wide tube, but afterwards the heat of the dish will always ignite the fresh piece as it is dropped in. The wide tube must be closed with a cork whilst the phosphorus is burning.

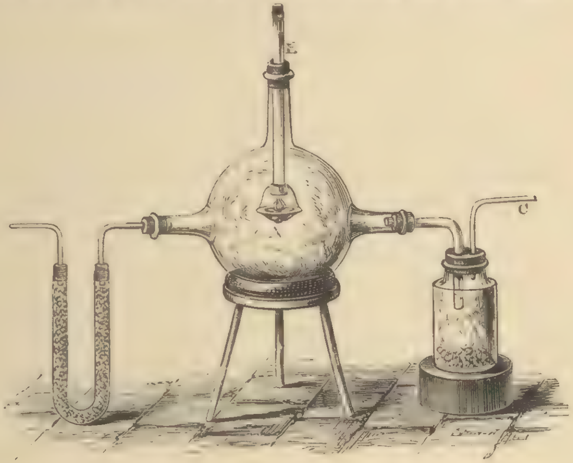

Fig. 211.

A small quantity of phosphoric anhydride is more conveniently prepared by burning phosphorus under a large bell-jar of air, under which a shallow dish of oil of vitriol has been standing for an hour or two to dry the air. This dish is carefully removed without disturbing the air within the jar, and the well-dried phosphorus is introduced in a small porcelain crucible standing upon a large glass plate. The phosphorus having been kindled with a hot wire, the flakes of phosphoric anhydride will be seen falling like snow on to the glass plate, where they accumulate in a layer of considerable thickness (fig. 212). To preserve it, the solid must be immediately scraped up with a bone or platinum knife, and thrown into a thoroughly dry stoppered bottle.

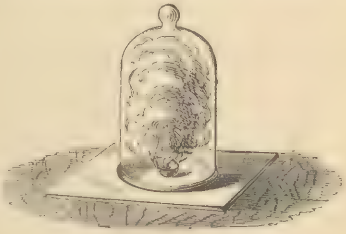

Fig. 212.

Phosphoric anhydride may be fused at a very high temperature, and even sublimed. Its great feature is its attraction for water; left exposed to the air for a very short time, it deliquesces entirely, becoming converted into phosphoric acid. It is often used by chemists as a *de-hydrating agent*, and will even remove water from oil of vitriol. When thrown into water, it hisses like a red-hot iron, but does not entirely dissolve at once, a few flakes of metaphosphoric acid remaining suspended in the liquid for some time.

The solution obtained by dissolving phosphoric anhydride in water contains *monohydrated phosphoric acid* or *metaphosphoric acid* ($H_2O.P_2O_5$ or HPO_3). If a little silver nitrate be added to a portion of it, a transparent gelatinous precipitate is formed, which is the silver metaphosphate ($AgNO_3 + HPO_3 = HNO_3 + AgPO_3$).

If the solution of metaphosphoric acid be heated in a flask for a short time, it will lose the property of yielding a precipitate with silver nitrate, unless one or two drops of ammonia be added to neutralise it, when an opaque white precipitate of silver pyrophosphate ($2Ag_2O.P_2O_5$ or $Ag_4P_2O_7$) is obtained, for the phosphoric acid has now been converted into the *dihydrated* or *pyrophosphoric acid* ($2H_2O.P_2O_5$ or $H_4P_2O_7$). The formation of the precipitate is thus expressed—

$$H_4P_2O_7 + 4AgNO_3 + 4NH_3 = Ag_4P_2O_7 + 4NH_4NO_3.$$

When the solution of pyrophosphoric acid is mixed with more water and boiled for a long time, it gives, when tested with silver nitrate and a little ammonia, a yellow precipitate of silver orthophosphate ($3Ag_2O.P_2O_5$ or Ag_3PO_4); the phosphoric acid having become converted into *trihydrated phosphoric acid* or *orthophosphoric acid* ($3H_2O.P_2O_5$ or H_3PO_4), and acting upon the silver nitrate in the presence of ammonia, thus—

$$H_3PO_4 + 3AgNO_3 + 3NH_3 = Ag_3PO_4 + 3NH_4NO_3.$$

The *pyrophosphoric acid* ($H_4P_2O_7$) cannot be obtained by the above process without an admixture of one of the other acids, but it has been obtained in crystals by decomposing the lead pyrophosphate ($Pb_2P_2O_7$) with hydrosulphuric acid, and evaporating the filtered solution *in vacuo* over oil of vitriol.

Trihydrated phosphoric acid may also be obtained in prismatic crystals by evaporating its solution in a similar way. This acid is also called *orthophosphoric acid* (*ὀρθός*, *true*), and *common* phosphoric acid, in allusion to the circumstance that the phosphates commonly met with and employed in the arts are the salts of this acid.

It will be perceived, from their formulæ, that metaphosphoric, HPO_3, orthophosphoric, H_3PO_4, and pyrophosphoric acid, $H_4P_2O_7$, are respectively monobasic, tribasic, and tetrabasic acids. The normal sodium salts of these acids are, respectively, metaphosphate, $NaPO_3$, orthophosphate, Na_3PO_4, and pyrophosphate, $Na_4P_2O_7$. The hydrogen in orthophosphoric and pyrophosphoric acids may be only partly replaced by a metal; thus there are two other orthophosphates of sodium, viz., hydrodisodic phosphate, HNa_2PO_4, and dihydrosodic phosphate, H_2NaPO_4.

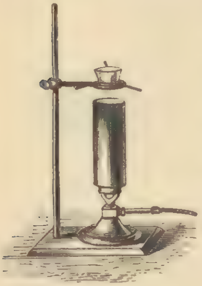
Fig. 213.

The phosphates commonly met with are all derived from orthophosphoric acid: for example, bone-ash, or tricalcic orthophosphate, $Ca_3(PO_4)_2$; superphosphate, or monocalcic orthophosphate, $CaH_4(PO_4)_2$; common phosphate of soda, or hydrodisodic orthophosphate, HNa_2PO_4; microcosmic salt, or hydro-ammonio-sodic orthophosphate, $HNH_4Na(PO_4)$.

Pyrophosphates and metaphosphates may be obtained by the action of heat on the hydro-orthophosphates.

Thus, if a crystal of the common rhombic sodium phosphate ($HNa_2PO_4.12Aq$) be heated gently in a crucible (fig. 213), it melts in its water of crystallisation, and gradually dries up to a white mass, the composition of which, if not heated beyond 300° F., will be Na_2HPO_4. If a little of this white mass be dissolved in water, the solution will be *alkaline* to red litmus-paper; and if silver nitrate (itself *neutral* to test-papers) be added to it, a *yellow* precipitate of silver orthophosphate will be obtained, and the solution will become strongly *acid*—

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

If the dried sodium phosphate be now strongly heated over a lamp, it will lose water, and become pyrophosphate (*πῦρ*, *fire*); $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. On dissolving this in water, the solution will be *alkaline*, and will give with silver nitrate a *white* precipitate and a *neutral* solution; $Na_4P_2O_7 + 4AgNO_3 = Ag_4P_2O_7 + 4NaNO_3$.

Microcosmic salt ($NaNH_4HPO_4.4Aq$), when dissolved in water, yields an *alkaline* solution which gives a *yellow* precipitate with silver nitrate, the liquid becoming *acid*; $NaNH_4HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + NH_4NO_3 + HNO_3$.

But if the salt be heated in a crucible, it fuses, evolving water and ammonia, and leaving a transparent glass of sodium metaphosphate; $NaNH_4HPO_4 = H_2O + NH_3 + NaPO_3$, which may be dissolved by soaking in water, yielding a slightly *acid* solution, which gives a *white* gelatinous precipitate with silver nitrate, the liquid being *neutral*; $NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3$.

All the phosphates may be converted into orthophosphates, by fusing them with alkaline hydrate or carbonate.*

164. *Phosphorous anhydride* (P_2O_3) is the product of the slow combustion of phosphorus. If a piece of phosphorus be heated in a long glass tube, into which a very slow current of dry air is drawn through a very narrow tube, it burns with a pale blue flame, and white flakes of phosphorous anhydride (mixed with P_2O_5) are deposited. It is more easily converted into vapour than phosphoric acid. It eagerly absorbs moisture from the air, and is decomposed when strongly heated in a sealed tube, yielding free phosphorus and phosphoric anhydride—

$$5P_2O_3 = 3P_2O_5 + P_4.$$

Phosphorus tetroxide, P_2O_4, corresponding to N_2O_4, is obtained as a very deliquescent crystalline sublimate by heating to about 290° C. in a sealed tube filled with CO_2, the mixture of P_2O_5 and P_2O_3 obtained by slowly burning phosphorus in dry air; the white mixture becomes orange, from the production of P_4O by the decomposition of the phosphorous anhydride; $7P_2O_3 = 5P_2O_4 + P_4O$. When dissolved in water it is converted into a mixture of phosphorous and orthophosphoric acids; $P_2O_4 + 3H_2O = H_3PO_4 + H_3PO_3$.

Phosphorous acid, H_3PO_3 or $PHO(OH)_2$, is obtained in solution, mixed with phosphoric acid, when sticks of phosphorus arranged in separate tubes open at both ends, and, placed in a funnel over a bottle, are exposed under a bell-jar, open at the top, to air saturated with aqueous vapour. To obtain the pure acid, chlorine is very slowly passed through phosphorus fused under water, when the phosphorous chloride first formed is decomposed by the water into phosphorous and hydrochloric acids; $PCl_3 + 3H_2O = PHO(OH)_2 + 3HCl$. The hydrochloric acid is expelled by a moderate heat, when the phosphorous acid is deposited in prismatic crystals. When heated, it is decomposed into phosphoric acid and gaseous phosphuretted hydrogen; $4H_3PO_3 = 3H_3PO_4 + PH_3$.

Solution of phosphorous acid gradually absorbs oxygen from the air, becoming phosphoric acid. This tendency to absorb oxygen causes it to act as a reducing agent upon many solutions; thus it precipitates finely divided metallic silver from a solution of the nitrate, by which its presence may be recognised in the water in which ordinary phosphorus has been kept. The solution of phosphorous acid even reduces sulphurous acid, producing sulphuretted hydrogen and sulphur, the latter being formed by the action of the sulphuretted hydrogen upon the sulphurous acid; $H_2SO_3 + 3H_3PO_3 = 3H_3PO_4 + H_2S$.

If solution of phosphorous acid be poured into a hydrogen apparatus, some hydric phosphide is formed which imparts a fine green tint to the hydrogen flame.

165. *Hypophosphorous acid*, H_3PO_2 or $HP(OH)_2$.—When phosphorus is boiled with barium hydrate and water, the latter is decomposed, its hydrogen combining with part of the phosphorus to form hydric phosphide (spontaneously inflammable), which escapes, whilst the oxygen of the water unites with another part of the phosphorus, forming hypophosphorous acid, which acts on the baryta to form barium hypophosphite; this may be obtained by evaporating the solution, in crystals having the composition $BaH_4(PO_2)_2$. The action of phosphorus upon barium hydrate may be represented by the equation—

$$\underset{\text{Barium hydrate.}}{3Ba(OH)_2} + 6H_2O + P_8 = \underset{\text{Barium hypophosphite.}}{3BaH_4(PO_2)_2} + 2PH_3.$$

Some barium orthophosphate is also formed at the same time, as the result of a secondary action.

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* It has been remarked that the *pliancy* of the acid character of phosphoric acid particularly fits it to take part in the vital phenomena. It may be regarded as three acids in one.

By dissolving the barium hypophosphite in water, and decomposing it with the requisite quantity of sulphuric acid, so as to precipitate the barium as sulphate, a solution is obtained which may be concentrated by careful evaporation. If this hypophosphorous acid be heated, it evolves hydric phosphide, and becomes converted into phosphoric acid; $2H_3PO_2 = H_3PO_4 + PH_3$. When exposed to the air it absorbs oxygen, and becomes converted into phosphorous and phosphoric acids. It is a more powerful reducing agent than phosphorous acid. The latter acid does not reduce a solution of cupric sulphate, but hypophosphorous acid, when gently warmed with it, gives a brown precipitate of *cuprous hydride* (CuH), which is decomposed by boiling, evolving hydrogen and leaving metallic copper.

When heated, the hypophosphites evolve hydric phosphide, and are converted into phosphates. The sodium hypophosphite, $NaP(OH)_2$, is sometimes used in medicine; its solution has been known to explode with great violence during evaporation, probably from a sudden disengagement of hydric phosphide. Hypophosphites, when boiled with caustic alkalies, are converted into phosphates, hydrogen being evolved; phosphites are unchanged.

The following is a summary of the *acids formed by phosphorus with oxygen and hydrogen*:—

Hypophosphorous acid	. . . . .	$P'''H(OH)_2$
Phosphorous ,,	. . . . .	$P'''HO(OH)_2$
Metaphosphoric ,,	. . . . .	$P^vO_2.OH$
Orthophosphoric ,,	. . . . .	$P^vO(OH)_3$
Pyrophosphoric ,,	. . . . .	$P^v{}_2O_3(OH)_4$

166. *Suboxide of phosphorus* is supposed to constitute the yellow or red residue which is left in the dish when phosphorus burns in air, but it is always mixed with much phosphoric anhydride. If phosphorus be melted under water in a flask (fig. 214), and oxygen gas be allowed to bubble through it (a brass tube being employed to convey the oxygen), each bubble of the gas produces a brilliant flash, and the phosphorus is converted into red flakes, which were believed to be suboxide of phosphorus, but are really amorphous phosphorus. The true suboxide of phosphorus (P_4O) appears to be formed when small pieces of phosphorus are covered with phosphorous chloride, exposed to the air, and afterwards heated with water, when the suboxide is deposited as a yellow powder becoming red at high temperatures, and inflaming when heated in air.

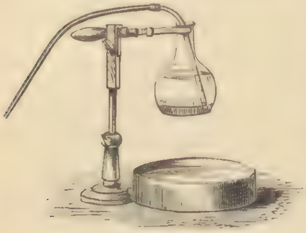

Fig. 214.

PHOSPHIDES OF HYDROGEN.

167. Although phosphorus and hydrogen do not combine directly, there are three compounds of these elements producible by processes of substitution, viz., PH_3, gas; P_2H_4, liquid; P_4H_2, solid.

Gaseous hydric phosphide, or *phosphuretted hydrogen gas*, or *phosphine* ($PH_3 = 34$ parts by weight $= 2$ volumes $= \frac{1}{2}$ volume $P + 3$ volumes H), is by far the most important of these. It has been mentioned above as resulting from the action of heat upon phosphorous acid, and when prepared by this process, it is obtained as a colourless gas, with a most powerful odour of putrid fish, inflaming on the approach of a light, and burning with a brilliant white flame, producing thick clouds of phosphorus pentoxide. It is slightly heavier than air (sp. gr. 1.19), and has been liquefied at − 90° C. and solidified at − 133° C.

The ordinary method of preparing this gas for experimental purposes consists in boiling phosphorus with a strong solution of potash, when water is decomposed, its hydrogen combining with one part of the phosphorus, and its oxygen with another part forming hypophosphorous acid, which unites with the potash—

$$P_4 + 3KHO + 3H_2O = PH_3 + 3KP(OH)_2.$$

A few fragments of phosphorus are introduced into a small retort (fig. 215), which is then nearly filled with a strong solution of potash (sp. gr. 1.3),* and heated. The extremity of the neck of the retort should not be plunged under water until the spontaneously inflammable gas is seen burning at the orifice, and the retort must not be placed close to the face of the operator, since explosions sometimes take place in preparing the gas, and the boiling potash produces dangerous effects. The gas may be collected in small jars filled with water, taking care that no bubble of air is left in them. It contains hydric phosphide mixed with free hydrogen, the latter being formed from the de-oxidation of water by the potassium hypophosphite. As each bubble of this gas escapes into the air through the water of the pneumatic trough, it burns with a vivid white flame, producing beautiful wreaths of smoke (phosphoric anhydride), resembling the *gunner's rings* sometimes seen in firing cannon. Small bubbles sometimes escape without spontaneously inflaming. If a bubble be sent up into a jar of oxygen, the flash of light is extremely vivid, and the jar must be a strong one to resist the concussion. It is advisable to add a trace of chlorine to the oxygen, to insure the inflammation of each bubble, for an accumulation of the gas would shatter the jar.

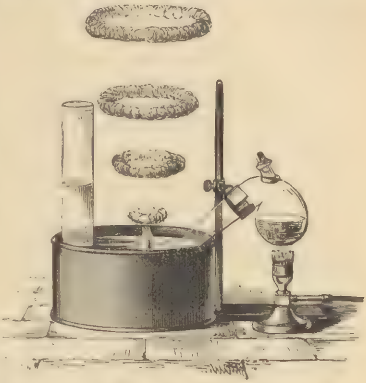

Fig. 215.—Preparation of phosphuretted hydrogen.

If this gas be passed through a tube cooled in a freezing mixture of ice and salt, the gas escaping from the tube is found to have lost its spontaneous inflammability, although it takes fire on contact with flame. The cold tube contains the *liquid hydric phosphide* (PH_2), which was present in the gas in the state of vapour, and caused its spontaneous inflammability, for as soon as the liquid comes in contact with air it takes fire. When exposed to light, the liquid phosphide is decomposed into the gaseous phosphide, and a yellow *solid phosphide* (P_4H_2), which is not spontaneously inflammable; $10PH_2 = P_4H_2 + 6PH_3$. It is for this reason that the spontaneously inflammable gas loses that property when kept (unless in the dark), depositing the solid phosphide upon the sides of the jar.

By passing a few drops of oil of turpentine up through the water into a jar of the spontaneously inflammable gas, this property will be entirely destroyed.

Hydric phosphide, when passed through solutions of some of the metals, precipitates their phosphides. For example, with cupric sulphate it gives a black precipitate of cupric phosphide; $3CuSO_4 + 2PH_3 = 3H_2SO_4 + P_2Cu_3$.

When this black precipitate is heated with solution of potassium cyanide, it evolves self-lighting hydric phosphide.† In fact, this is one of the easiest and safest methods of preparing this gas; for the cupric phosphide is readily obtained by simply boiling phosphorus in a solution of cupric sulphate.

Phosphine is absorbed by strong sulphuric acid, and, after a time, acts upon it with great evolution of heat, SO_2 being formed and sulphur deposited. Sulphur decomposes it in sunshine; $2PH_3 + S_6 = P_2S_3 + 3H_2S$.

Phosphine has great pretensions to rank as the chemical analogue of ammonia, for although it has no alkaline properties, it is capable of combining with hydrobromic and hydriodic acids to form crystalline compounds analogous to ammonium bromide and iodide; these compounds, however, are decomposed by water. It will be seen hereafter, that when the hydrogen in phosphine is displaced by certain compound radicals, such as ethyle, powerful organic bases are produced.

The spontaneously inflammable hydric phosphide may also be obtained by throwing fragments of *calcium phosphide* into water; this substance is prepared by passing vapour of phosphorus over red-hot quicklime, or simply by heating small lumps of quicklime to bright redness in a crucible and throwing in fragments of phosphorus, closing the crucible immediately. The dark brown mass thus obtained is a mixture of pyrophosphate and phosphide of calcium, of somewhat variable composition.

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* 450 grains of common stick potash dissolved in 1000 grains of water, or 45 grms. in 100 c.c.

† Cupric cyanide and potassium phosphide being formed, and the latter decomposed by water, giving hydric phosphide and potassium hypophosphite.

The calcium phosphide has been used in life-buoys for indicating by the flare their position on the water.

When phosphine is decomposed by a succession of electric sparks, 2 volumes of the gas yield 3 volumes of hydrogen, the phosphorus being deposited in the red or amorphous form.

168. Two *chlorides of phosphorus* are known. The *trichloride* or *phosphorous chloride* (PCl_3) is prepared by acting upon phosphorus with perfectly dry chlorine in the apparatus employed (p. 217) for preparing the chloride of sulphur. Red phosphorus may be used, and the product redistilled with a little vitreous phosphorus to decompose any PCl_5. Phosphorous chloride distils over very easily (boiling point, 173° F. or 78° C.), as a colourless, pungent liquid (sp. gr. 1.62), which fumes strongly in air, its vapour decomposing the moisture of the air and producing hydrochloric acid fumes. In contact with water the liquid is immediately decomposed, yielding hydrochloric and phosphorous acids, as described for the preparation of the latter acid (p. 231). Its analogy to phosphorous anhydride is shown by its absorbing oxygen when boiled in the presence of that gas, and forming the *phosphorus oxychloride* or *phosphoryle chloride*, $POCl_3$. It also absorbs chlorine with avidity, becoming converted into *pentachloride of phosphorus* or *phosphoric chloride* (PCl_5). This compound, however, is more conveniently prepared by passing chlorine through a solution of phosphorus in carbon disulphide, carefully cooled. On evaporation, the pentachloride of phosphorus is deposited in white prismatic crystals, which volatilise below 212° F., and fume when exposed to air, from the production of hydrochloric acid. When thrown into water, it is decomposed into phosphoric and hydrochloric acids; $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$. But if it be allowed to deliquesce in air, only a partial decomposition takes place, and the phosphorus oxychloride is formed; $PCl_5 + H_2O = PCl_3O + 2HCl$. The same compound is obtained by distilling P_2O_5 with NaCl—

$$2P_2O_5 \ + \ 3NaCl \ = \ POCl_3 \ + \ 3NaPO_3.$$

This oxychloride may also be produced by heating phosphoric chloride with phosphoric anhydride; $P_2O_5 + 3PCl_5 = 5PCl_3O$. A more instructive method of preparing it consists in distilling the phosphoric chloride with crystallised boric acid; $3PCl_5 + 2B(OH)_3 = 3PCl_3O + 6HCl + B_2O_3$.

Some of the organic acids (succinic, for example) may be converted into anhydrides, as the boric acid is in this case, by distilling with phosphoric chloride. The phosphorus oxychloride distils over (boiling point, 230° F., 110° C.) as a heavy (sp. gr. 1.7) colourless fuming liquid of pungent odour. Of course, it is decomposed by water, yielding hydrochloric and phosphoric acids. It will be found of the greatest use in effecting certain transformations in organic substances.

The analogy between water and hydrosulphuric acid would lead to the expectation that a *sulphochloride of phosphorus* (PCl_3S), corresponding to the oxychloride, would be formed by the action of hydrosulphuric acid upon phosphoric chloride; $PCl_5 + H_2S = PCl_3S + 2HCl$. It is a colourless fuming liquid, which is slowly decomposed by water, giving phosphoric, hydrochloric, and hydrosulphuric acids; $PCl_3S + 4H_2O = H_3PO_4 + 3HCl + H_2S$. When acted on by solution of soda, the sulphochloride of phosphorus loses its chlorine to the sodium, and acquires an equivalent quantity of oxygen, a sodium *sulphoxy-phosphate* ($Na_3PO_3S.12H_2O$) being deposited in crystals. This salt evidently corresponds in composition to the sodium orthophosphate ($Na_3PO_4.12H_2O$), and its production is expressed by the equation, $PCl_3S + 6NaHO = 3NaCl + Na_3PO_3S + 3H_2O$. Salts of similar composition may be obtained with other metallic oxides.

When PCl_5 is heated above 148° C. it is dissociated into PCl_3 and Cl_2, but this may be prevented by surrounding it with an atmosphere of PCl_3, and thus its vapour density has been determined.

The *bromides* and *oxybromide of phosphorus* correspond to the chlorine compounds.

Iodine in the solid state combines very energetically with phosphorus, but if the two elements be brought together in a state of solution in carbon disulphide, a more moderate action ensues, and two *iodides of phosphorus* may be obtained in crystals; a tri-iodide (PI_3) corresponding to the trichloride, and diphosphorus tetriodide (P_2I_4), which has no analogue either among the oxygen, chlorine, or bromine compounds of phosphorus. P_2I_4 forms orange-red crystals which are decomposed by water, with separation of red phosphorus; $3P_2I_4 + 12H_2O = 12HI + P_2 + 4P(OH)_3$. PI_5 and PF_5 have also been obtained. The latter is a colourless gas.

The addition of a very small quantity of iodine to ordinary phosphorus, fused in a flask filled with carbonic acid gas, materially accelerates its conversion into the red modification, and allows the change to be effected at a much lower temperature than that required when the phosphorus is heated alone, probably because successive portions of vitreous phosphorus combine with the iodine to form an unstable iodide from which the heat separates the phosphorus in the amorphous form.

169. The *sulphides of phosphorus* may be formed by the direct combination of their elements. If ordinary phosphorus be used, the experiment is not unattended with danger, and should be performed under water. It is safer to combine the amorphous phosphorus with sulphur, at a moderate heat, in an atmosphere of carbonic acid gas.

P_4S_3 crystallises from carbon disulphide in yellow prisms, which are decomposed when boiled with water; $P_4S_3 + 9H_2O = 3P(OH)_3 + PH_3 + 3H_2S$.

P_2S_3 may be produced by the action of $3H_2S$ on $2PCl_3$; it is a yellow fusible solid which may be sublimed in crystals if air be excluded. Water decomposes it into phosphorous and hydrosulphuric acids; $P_2S_3 + 6H_2O = 2P(OH)_3 + 3H_2S$.

P_2S_5 forms pale yellow crystals which yield phosphoric acid when decomposed by water; $P_2S_5 + 8H_2O = 2PO(OH)_3 + 5H_2S$. It is used for replacing O by S in organic compounds. It combines with alkaline sulphides, forming *sulphophosphates;* $3K_2S + P_2S_5 = 2K_3PS_4$.

P_2S is a yellow oily liquid which may be distilled out of contact with air, and is not decomposed by water.

P_2S_4 forms yellow crystals.

170. *Phosphamides* or *amides of phosphoric acid.*—When phosphorus oxychloride is acted on by ammonia, ammonium chloride and *phosphotriamide* are produced; the former is dissolved by water, which leaves the phosphotriamide as a white insoluble body, not easily attacked by acids and alkalies—

$$PCl_3O + 6NH_3 = 3NH_4Cl + N_3H_6PO \text{ (\textit{phosphotriamide})}.$$

If the sulphochloride, PCl_3S, be substituted for the oxychloride, the corresponding *sulphosphotriamide*, N_3H_6PS, is obtained.

The action of ammonia on phosphoric chloride yields *chlorophosphamide*, $N_2H_4PCl_3$; $PCl_5 + 2NH_3 = 2HCl + N_2H_4PCl_3$.

When this is boiled with water, a very stable insoluble substance is obtained, which is *phosphodiamide;* $N_2H_4PCl_3 + H_2O = 3HCl + N_2H_3PO$ (*phosphodiamide*).

When heated, it evolves ammonia and becomes *phosphonitrile*—

$$N_2H_3PO = NH_3 + NPO.$$

The phosphamides may be regarded as being derived from the ammonium orthophosphates by the abstraction of $3H_2O$; thus—

$(NH_4)_3PO_4$ *minus* $3H_2O$ = N_3H_6PO or $PO(NH_2)_3$, Phosphotriamide.
$(NH_4)_2HPO_4$,, ,, = N_2H_3PO or $PO(NH_2)NH$, Phosphamide-imide.
$NH_4H_2PO_4$,, ,, = NPO, Phosphonitrile.

When boiled with potassium hydrate, the phosphamides acquire the elements of water, and are converted into ammonia and potassium orthophosphate.

Nitrogen chlorophosphide, $N^{v}{}_3P'''{}_3Cl_6$, is obtained by distilling phosphoric chloride with ammonium chloride; $3PCl_5 + 3NH_4Cl = N_3P_3Cl_6 + 12HCl$. It is a crystalline solid, insoluble in water, and slowly decomposed by it; $2P_3N_3Cl_6 + 15H_2O = 12HCl + 3P_2O_3(NH_2)_2(OH)_2$, *pyrophosphodiamic acid*, or pyrophosphoric acid, $P_2O_3(OH)_4$, in which two NH_2 groups have replaced two OH groups.

ARSENIC.

As=75 parts by weight.*

171. This element is often classed among the metals, because it has a metallic lustre and conducts electricity, but it is not capable of forming a base with oxygen, and the chemical character and composition of its compounds connect it in the closest manner with phosphorus.

In its mode of occurrence in nature it more nearly resembles the sulphur group of elements, for it is occasionally found in the uncombined state (*native arsenic*), but far more abundantly in combination with various metals, forming *arsenides*, which frequently accompany the sulphides of the same metals. The following are some of the chief arsenides and *arsenio-sulphides* found in the mineral kingdom :—

Kupfernickel	$NiAs$	Mispickel	$FeS_2.FeAs_2$
Arsenical nickel	$NiAs_2$	Cobalt-glance	$CoS_2.CoAs_2$
Tin-white cobalt	$CoAs_2$	Nickel-glance	$NiS_2.NiAs_2$
Arsenical iron	Fe_2As_3		

But arsenic also occurs, like the metals, in combination with sulphur; thus we have red orpiment or realgar, As_2S_2, and yellow orpiment, As_2S_3. It is from these minerals that arsenic derives its name (ἀρσενικὸν, *orpiment*); the sulphides of arsenic are also found in combination with other sulphides: thus *Proustite* is a compound of the sulphides of silver and arsenic ($3Ag_2S.As_2S_3$); *Tennantite* contains sulphide of arsenic combined with the sulphides of iron and copper; and *grey copper ore* is composed of sulphide of arsenic with the sulphides of copper, silver, zinc, iron, and antimony. In an oxidised form arsenic is found in *condurrite*, which contains arsenious anhydride (As_2O_3) and cuprous oxide. *Cobalt-bloom* consists of cobalt arsenate, $Co_3(AsO_4)_2$.

Arsenical pyrites is one of the principal sources of arsenic and its compounds, though a considerable quantity is also obtained in the form of arsenious oxide as a secondary product in the working of certain ores, especially those of copper, tin, cobalt, and nickel.

The substance used in the arts under the name of arsenic is really the arsenious oxide (As_2O_3); pure arsenic itself has very few useful applications, so that it is not the subject of an extensive manufacture. It can be extracted from *mispickel* ($Fe_2S_2As_2$) by heating it in earthen cylinders fitted with iron receivers, in which the arsenic condenses as a metallic-looking crust, the heat expelling it from the mineral in the form of vapour.

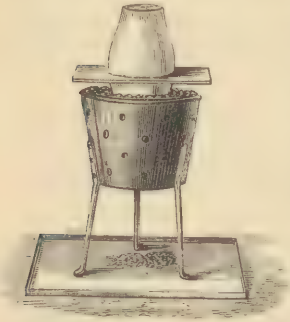

Fig. 216.—Extraction of arsenic.

On a small scale it may be obtained by heating a mixture of white arsenic with half its weight of recently calcined charcoal in a crucible (fig. 216), the mixture being covered with two or three inches of charcoal in very small fragments, and the crucible so placed that this charcoal may be heated to redness first, in order to ensure the reduction of any oxide which might escape from below. In order to collect the arsenic, another crucible, having a small hole drilled through the bottom for the escape of gas, is cemented on to the first, in an inverted position, with fire-clay, and protected from the fire by an iron plate with a hole in it for the crucible. The reduction of arsenious anhydride by charcoal is thus represented—

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* The specific gravity of the vapour of arsenic, like that of phosphorus, indicates that 75 parts by weight only occupy half a volume. Hence the molecule of arsenic must be represented as As_4 = 2 volumes; but at very high temperatures a disposition to conform with the law is shown by a diminution in the vapour density.

$$As_2O_3 + C_3 = As_2 + 3CO.$$

For the sake of illustration, a small quantity of arsenic may be prepared from white arsenic by a method commonly employed in testing for that substance. A small tube of German glass is drawn out to a narrow point (A, fig. 217), and sealed with the aid of the blowpipe. A very minute quantity of white arsenic is introduced into the point of the tube, and a few fragments of charcoal are placed in the tube itself at B The charcoal is heated to redness with a blowpipe flame, and the point is then heated so as to drive the white arsenic in vapour over the red-hot charcoal, when a shining black ring of arsenic (C) will be deposited upon the cooler portion of the tube.

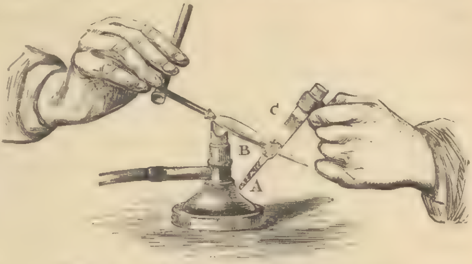

Fig. 217.—Reduction of arsenious oxide.

The arsenic thus obtained is a brittle mass of a dark steel-grey colour and brilliant metallic lustre (sp. gr. 5.7). It does not fuse when heated, unless in a sealed tube, since it is converted into vapour at 180° C. It is not changed by exposure to air, unless powdered and moistened, when it is slowly converted into As_2O_3. When heated in air it oxidises rapidly at about 71° C., giving off white fumes of arsenious oxide and a characteristic garlic odour (recalling that of phosphorus), which is also produced when arsenical pyrites is struck with a hammer or pick. At a red heat it burns in air with a bluish-white flame, and in oxygen with great brilliancy. It is not dissolved by water or any simple solvent, but is oxidised and dissolved by nitric acid.

In its chemical relations to other elements, arsenic much resembles phosphorus, undergoing spontaneous combustion in chlorine, and easily combining with sulphur. Like phosphorus also, it combines with many metals, even with platinum, to form arsenides, and its presence often affects materially the properties of the useful metals.

Pure arsenic does not produce symptoms of poisoning till a considerable period after its administration, being probably first oxidised in the stomach and intestines, and converted into arsenious acid.

When arsenic is sublimed in a tube filled with hydrogen, ordinary or crystalline arsenic condenses on the warmer part of the tube, but, on the cooler part, *amorphous arsenic* is deposited, of sp. gr. only 4.7. This is not so easily oxidised in moist air as the crystalline variety. At 360° C. it evolves heat and becomes converted into crystalline arsenic.

OXIDES OF ARSENIC.

172. Arsenic forms two compounds with oxygen, corresponding to phosphorous and phosphoric anhydrides, viz., As_2O_3 and As_2O_5.

ARSENIOUS OXIDE (As_2O_3 = 198 parts by weight = 1 volume = 1 volume As + 3 volumes O).*—Unlike phosphorus, arsenic, when burning in air, only combines with three atoms of oxygen. Arsenious oxide, or *white arsenic*, is a very useful substance in many branches of industry. It is employed in the manufacture of glass, and of several colouring matters. A large quantity is also consumed for the preparation of arsenic acid and arseniate of soda; it is, indeed, the source from which nearly all the compounds of arsenic are procured. Small quantities of crystalline arsenious oxide are occasionally found associated with the ores of nickel and cobalt.

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* The specific gravity of the vapour of arsenious oxide is 198 times that of hydrogen, instead of 99 times according to the usual law.

White arsenic is manufactured by roasting the arsenical pyrites, chiefly obtained from the mines of Silesia, in *muffles* or ovens, through which air is allowed to pass, when the arsenic is converted into As_2O_3, and the sulphur into SO_2, which are conducted into large chambers in which the As_2O_3 is deposited as a very fine powder. The iron of the pyrites is left partly as oxide, and partly as sulphate of iron. The removal of the As_2O_3 from the condensing chambers is a very unwholesome operation, owing to its dusty and very poisonous character. The workmen are cased in leather, and protect their mouths and noses with damp cloths, so as to avoid inhaling the fine powder.

This rough white arsenic is subjected to a second sublimation on a smaller scale in iron vessels, when it is obtained in the form of a semi-transparent glassy mass known as *vitreous arsenious acid*, which gradually becomes opaque when kept, and ultimately resembles porcelain. The white arsenic sold in the shops is a fine powder, dangerously resembling flour in appearance, but so much heavier (sp. gr. 3.8) that it ought not to be mistaken for it. When examined under the microscope, it appears in the form of irregular glassy fragments, mixed with octahedral crystals. White arsenic softens when gently heated, but does not fuse (unless in a sealed tube), being converted into vapour at 193° C., and depositing in brilliant octahedral crystals upon a cool surface. The experiment may be made in a small tube sealed at one end, the upper part of which should be slightly warmed before heating the arsenious oxide, so as to prevent too rapid condensation, which is unfavourable to the formation of distinct crystals.* The octahedra are best examined with a binocular microscope. This common poison may fortunately be still more easily recognised by sprinkling it upon a red-hot coal, when a strong odour of garlic is perceptible, due to the reduction of the As_2O_3 by the heated carbon; the vapour of white arsenic itself is inodorous. The sparing solubility of white arsenic in water is very unfavourable to its action as a poison, for, when thrown into ordinary liquids, it is dissolved in very small quantity, the greater part of it collecting at the bottom. Even when taken into the stomach in a solid state, its want of solubility delays its operation sufficiently to give a better chance of antidotal treatment than in the case of most other common poisons. Its comparative insolubility is shown by its being almost tasteless.

When thrown into water, white arsenic exhibits great repulsion for the particles of that liquid, and collects in a characteristic manner round little bubbles of air, forming small white globes which are not wetted by the water. Even if stirred with the water, and allowed to remain in contact with it for some hours, a pint of water (20 oz.) would not take up more than 20 grs. The smallest dose which has been known to prove fatal is 2.5 grs. If boiling water be poured upon powdered white arsenic, and allowed to remain in contact with it till cold, it will dissolve about $\frac{1}{400}$th of its weight (22 grs. in a pint).

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* When arsenious oxide is fused in a long tube, sealed at both ends, and buried in hot sand, the mass, after cooling, is found to contain some prismatic crystals, which are also sublimed on those parts of the tube which have been heated above 200° C.

When powdered white arsenic is boiled with water for two or three hours, 100 parts by weight of water may be made to dissolve 11.5 parts, and when the solution is allowed to cool, about 9 parts will be deposited in octahedral crystals, leaving 2.5 parts dissolved in 100 of water (219 grs. in a pint).

This great increase in the solubility of the arsenious oxide by long boiling with water is usually attributed to the conversion of the opaque or crystalline variety, which always composes the powder, into the vitreous modification, which is the more soluble in water. Water, heated with white arsenic in a sealed tube, may be made to dissolve its own weight of it; as the solution cools, it first deposits prismatic crystals, and afterwards the ordinary octahedral form. The solution is very feebly acid to blue litmus-paper. Glycerin dissolves As_2O_3 easily when heated.

White arsenic dissolves abundantly in hot hydrochloric acid (a part of it being converted into arsenious chloride), and as the solution cools, part of the oxide is deposited in large octahedral crystals. It is said that if the vitreous form be dissolved in hydrochloric acid, the formation of these crystals will be attended by flashes of light, visible in a darkened room; but the opaque variety does not exhibit this phenomenon.

The vitreous arsenious oxide has specific gravity 3.798, and the opaque 3.529, and the former fuses rather more easily. The opaque variety appears to be identical in its properties with crystallised arsenious oxide.

Solutions of the alkalies readily dissolve arsenious oxide, forming alkaline arsenites, the solutions of which are capable of dissolving arsenious oxide more easily than water, and deposit it in crystals on cooling. Arsenious oxide is sometimes deposited in *prismatic* crystals from its solution in potash, and the same form has been found native. On adding a small quantity of hydrochloric acid to the solution of the alkaline arsenite, a white precipitate of arsenious oxide is formed.

White arsenic has the property of preventing the putrefaction of skin and similar substances, and is occasionally employed for the preservation of objects of natural history, &c.

Arsenites.—Arsenious acid, properly so called, has not yet been obtained in the separate state. The aqueous solution of white arsenic, when neutralised exactly with ammonia, yields, with silver nitrate, a yellow precipitate having the composition Ag'_3AsO_3; with cupric sulphate, a green precipitate having the composition $Cu''HAsO_3$; with zinc sulphate, a white precipitate containing $Zn''_3(AsO_3)_2$; and with magnesium sulphate, a white precipitate of $Mg''HAsO_3$. It would appear, therefore, that the *arsenious acid* from which these salts are derived is a tribasic acid having the formula H_3AsO_3, corresponding to boric acid, H_3BO_3. Arsenious acid does not destroy the alkaline reaction of the alkalies, and it does not decompose the alkaline carbonates unless heat is applied, proving it to be a feeble acid. The ammonium arsenite is very unstable, evolving ammonia freely when exposed to the air. When arsenious oxide is dissolved in a hot solution of ammonia, octahedral crystals of it are deposited on cooling, notwithstanding the presence of ammonia in large excess.

When the carbonates of potassium and sodium are fused with an excess of arsenious oxide, brilliant transparent glasses are obtained which are similar in composition to glass of borax ($K_2As_4O_7$ and $Na_2As_4O_7$).

If an alkaline arsenite be fused in contact with platinum, the latter is easily melted, combining with a small proportion of arsenic to form a fusible platinum arsenide, a portion of the arsenite being converted into arsenate. The alkaline arsenates are so much more stable than the arsenites that the latter exhibit a great tendency to pass into the former, with separation of arsenic.

The arsenites of potassium and sodium in solution are sometimes employed as sheep-dipping compositions; and an arsenical soap, composed of potassium arsenite, soap, and camphor, is used by naturalists to preserve the skins of animals. Sodium arsenite is also occasionally employed for preventing incrustations in steam-boilers, being prepared for that purpose by dissolving 2 molecules of white arsenic and 1 molecule of sodium carbonate.

Scheele's green is an arsenite of copper prepared by dissolving white arsenic in a solution of potassium carbonate, and decomposing the arsenite of potassium thus produced by adding sulphate of copper, when the arsenite of copper is precipitated. This poisonous colour is used to impart a bright green tint to paper hangings, and is sometimes injurious to the health of the occupants of rooms thus decorated, since the arsenite of copper is often easily rubbed off the paper, and diffused through the air in the form of a fine dust, a small portion of which is inhaled with every breath.

The presence of the arsenite of copper in a sample of such paper is readily proved by soaking it in a little ammonia, which will dissolve the arsenite of copper to a blue liquid, the presence of arsenic in which may be shown by acidifying it with a little pure hydrochloric acid, and boiling with one or two strips of pure copper, which will become covered with a steel-grey coating of arsenide of copper. On washing the copper, drying it on filter-paper, and heating it in a small tube (fig. 218), the arsenic will be converted into arsenious oxide, which will deposit in brilliant octahedral crystals on the cool part of the tube. It is obvious that, to avoid mistakes, the ammonia, hydrochloric acid, and copper should be examined in precisely the same way, without the suspected paper, so so as to render it certain that the arsenic is not derived from them.

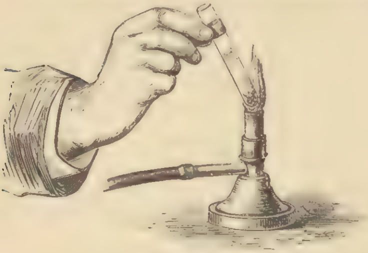

Fig. 218.

The effective green colour of the arsenite of copper also leads to its employment as a colour for feathers, muslin, &c., where it is very injurious to the health of the work-people. It has even been ignorantly or recklessly used for colouring twelfth-cake ornaments, &c.

Emerald-green is a combination of arsenite and acetate of copper obtained by mixing hot solutions of equal weights of white arsenic and acetate of copper.

In quantities short of poisonous doses, white arsenic appears to have a remarkable effect upon the animal body. Grooms occasionally employ it to improve the appearance of horses, and in Styria it seems to be taken by men and women for the same purpose, apparently favouring the secretion of fat. It is said that a continuance of the custom develops a craving for this drug, and enables large doses to be taken without immediate danger, though the ultimate consequences are very serious.

Solution of potassium arsenite (*Fowler's solution*) has long been used in medicine.

173. *Arsenic acid* (H_3AsO_4).—This acid has acquired great importance in the chemical arts during the last few years, having been employed to replace the expensive tartaric acid used in calico-printing, and to furnish, by its action upon aniline, the magnificent dye known as *Magenta*.

Arsenic acid is prepared by oxidising white arsenic with three-fourths of its weight of nitric acid of sp. gr. 1.35, when it dissolves with evolution of much heat and abundant red fumes of nitrous anhydride—

$$As_2O_3 + 2HNO_3 + 2H_2O = N_2O_3 + 2H_3AsO_4.$$

After cooling, the solution deposits very deliquescent prismatic crystals containing $2H_3AsO_4.Aq$. When heated to 100° C., these melt, and the liquid deposits needle-like crystals of *ortho-arsenic acid*, H_3AsO_4, corresponding to orthophosphoric; at 180° C., $2H_3AsO_4 = H_2O + H_4As_2O_7$, *pyro-arsenic acid*, corresponding to pyrophosphoric; at 206° C., $H_4As_2O_7 = H_2O + 2HAsO_3$, *metarsenic acid*, corresponding to metaphosphoric; but here the resemblance ceases, for at 260° C., $2HAsO_3 = H_2O + As_2O_5$, whereas HPO_3 may be vaporised without decomposition. When metarsenic and pyro-arsenic acids are dissolved in water, they at once become ortho-arsenic acid. The meta- and pyro-arsenates are known only in the solid state. As_2O_5 is decomposed at a red heat into As_2O_3 and O_2.

Arsenic anhydride, As_2O_5, has very much less attraction for water than the phosphoric anhydride to which it corresponds; it deliquesces slowly in air, and dissolves rather reluctantly in water. Neither does it appear that its combinations with water differ from each other, like the phosphoric acids, in the salts to which they give rise, arsenic acid forming tribasic salts only, like common phosphoric acid. The arsenates correspond very closely to the orthophosphates, with which they are isomorphous (*i.e.*, identical in crystalline form). Thus the three arsenates of sodium are similar in composition to the three orthophosphates, their formulæ being $Na_3AsO_4.12Aq$; $Na_2HAsO_4.12Aq$; and $2(NaH_2AsO_4)Aq$.

The common arsenate of soda ($Na_2HAsO_4.7Aq$) is largely used by calico-printers as a substitute for the dung-baths formerly employed, since, like the common phosphate of soda, it possesses the feebly alkaline properties required in that particular part of the process. It is manufactured by combining arsenious oxide with soda, and heating the resulting arsenite with sodium nitrate, from which it acquires oxygen, becoming converted into sodium arsenate.

Calcium arsenate, $2CaHAsO_4.7H_2O$, has been found in crystalline crusts at Joachimsthal. *Arsenio-siderite* and *xantho-siderite* are calcic-ferric arsenates.

Arsenic acid is a much more powerful acid than arsenious acid, being comparable, in this respect, with phosphoric acid. It is less stable than phosphoric acid, and acts as an oxidising agent. Sulphurous acid, which is without action on phosphoric, reduces arsenic acid to arsenious acid; $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$.

174. *Arsenetted hydrogen*, or *hydric arsenide* ($AsH_3 = 78$ parts by weight $= 2$ vols. $= \frac{1}{2}$ vol. $As + 3$ vols. H).—The only compound of arsenic and hydrogen the existence of which has been satisfactorily established is that which corresponds to ammonia and phosphine. It is prepared by the action of sulphuric acid diluted with three parts of water upon the zinc arsenide, obtained by heating equal weights of zinc and arsenic in an earthen retort; $Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$. The gas is so poisonous in its character that its preparation in the pure state is attended with danger. It has a sickly alliaceous odour, and may be liquefied at − 55° C. and solidified at − 119° C. It is inflammable, burning with a peculiar livid flame, producing water and fumes of arsenious oxide; $2AsH_3 + O_6 = As_2O_3 + 3H_2O$. The chief interest attaching to this gas depends upon the circumstance that its production allows of the detection of very minute quantities of arsenic in cases of poisoning.

The application of this test, known as Marsh's test, is the safest method of preparing arsenetted hydrogen in order to study its properties, for it is obtained so largely diluted with free hydrogen that it ceases to be so very dangerous. Some fragments of granulated zinc are introduced into a half-pint bottle (fig. 219), provided with a funnel tube (A), and a narrow tube (B) bent at right angles and drawn out to a jet at the extremity; this tube should be made of German glass, so that it may not fuse easily. The bottle having been about one-third filled with water, a little diluted sulphuric acid is poured down the funnel tube so as to cause a moderate evolution of hydrogen, and after about five minutes (to allow the escape of the air) the hydrogen is kindled at the jet. If a few drops of a solution obtained by boiling white arsenic with water be now poured down the funnel, arsenetted hydrogen will be evolved together with the hydrogen—

$$As_2O_3 + Zn_6 + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O.$$

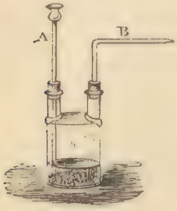

Fig. 219.

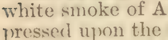

Fig. 220.

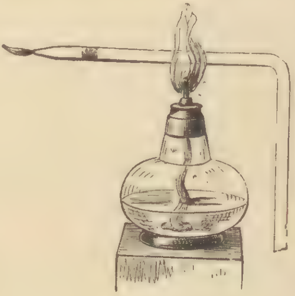

Fig. 221.

The hydrogen flame will now acquire the livid hue above referred to, and a white smoke of As_2O_3 will rise from it. If a piece of glass or porcelain be depressed upon the flame (fig. 220), it will acquire a brown coating of arsenic, just as carbon would be deposited from an ordinary gas-flame. Arsenetted hydrogen is easily decomposed by heat, so that if the glass tube through which it passes be heated with a spirit-lamp (fig. 221) a dark *mirror* of arsenic will be deposited a little in front of the heated part, and the flame of the gas will lose its livid hue. These deposits of arsenic are extremely thin, so that a very minute quantity of arsenic is required to form them, thus rendering the test one of extraordinary delicacy. It must be remembered, however, that both sulphuric acid and zinc are liable to contain arsenic, so that erroneous results may be very easily arrived at by this test.

Arsenetted hydrogen, like sulphuretted hydrogen, causes dark precipitates in many metallic solutions.

Silver nitrate is reduced to the metallic state by AsH_3; $AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 3Ag_2$. A piece of filter-paper, spotted over with silver nitrate solution, will have the spots blackened if held before the tube from which the gas issues. The simplest test for arsenic in wall-paper, &c., is to drop a piece of the paper into a glass containing some zinc and sulphuric acid, and to cover the mouth of the glass with a piece of paper wetted with silver nitrate, which will be blackened if arsenic be present. The purity of the materials should be tested first in the same way, and the absence of sulphur, which also blackens silver nitrate, should be proved by lead acetate, which is not blackened by arsenic.

Hydric phosphide, hydric arsenide, and ammonia constitute a group of hydrogen compounds having certain properties in common, which distinguish them from the compounds of hydrogen with other elements.

Two volumes of each of these gases contain three volumes of hydrogen.

They are all possessed of peculiar odours, that of ammonia being the most powerful and that of hydric arsenide the least. Ammonia is powerfully alkaline, phosphine exhibits some tendency to play an alkaline part, whilst hydric arsenide seems devoid of alkaline disposition. All these are inflammable, ammonia being the least so of the group; and all are decomposed by heat, ammonia least easily, and hydric arsenide most easily. They are all producible from their corresponding oxygen compounds, viz., N_2O_3, P_2O_3, and As_2O_3, by the action of nascent hydrogen (*e.g.*, by contact with zinc and diluted sulphuric acid).

All three are the prototypes of various organic bases which contain some compound radical in place of the hydrogen, thus—

NH_3 is the prototype of triethylamine $N(C_2H_5)_3$
PH_3 ,, ,, triethylphosphine $P(C_2H_5)_3$
AsH_3 ,, ,, triethylarsine $As(C_2H_5)_3$

175. *Arsenic trichloride*, or *arsenious chloride*.—Only one compound of chlorine with arsenic ($AsCl_3$) is well known.* The trichloride may be formed by the direct union of its elements, but the simplest laboratory process for procuring it consists in heating white arsenic in dry chlorine gas, in a tubulated retort (A, fig. 222), extemporised from a Florence flask (see p. 106). The arsenious anhydride soon melts, and the trichloride distils over, leaving a melted mass in the flask, which forms a brilliantly transparent glass on cooling, the composition of which varies somewhat with the temperature employed, but appears to be essentially $2As_2O_3.As_2O_5$. The same vitreous compound may be obtained by fusing arsenious and arsenic oxides together. The reaction may be represented by the equation, $11As_2O_3 + Cl_{12} = 4AsCl_3 + 3(2As_2O_3.As_2O_5)$.

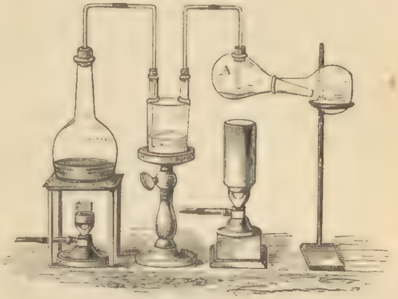

Fig. 222.

Arsenic trichloride bears a great general resemblance to phosphorus trichloride; it is a heavy (sp. gr. 2.2), pungent, fuming liquid, decomposed by the moisture of the air, its vapours depositing a white coating upon the objects in its immediate neighbourhood. When poured into water it deposits arsenious oxide; $2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$; but when dissolved in the smallest possible quantity of water it deposits crystals of the formula $AsOCl.H_2O$ or $AsCl(HO)_2$.

When white arsenic is dissolved in hydrochloric acid, arsenious chloride is formed, $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$, and remains undecomposed by the water in the presence of strong hydrochloric acid, but if water be added, arsenious oxide is precipitated. When the solution in hydrochloric acid is distilled, the arsenious chloride distils over, and this is sometimes a convenient method of separating arsenic from articles of food, &c., in testing for that poison. When heated in dry hydrochloric acid gas, white arsenic yields a glassy compound, which contains $As_2O_3.AsClO$; $3As_2O_3 + 2HCl = 2(As_2O_3.AsClO) + H_2O$.

Arsenic trichloride and arsenic trihydride decompose each other, yielding hydrochloric acid and arsenic.

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* Nicklés appears to have succeeded in forming the pentachloride by the action of hydrochloric acid gas on As_2O_5 in presence of ether; he describes it as very unstable, and easily converted into the trichloride.

In composition by volume, the arsenious chloride resembles phosphorous chloride, containing ½ volume of arsenic vapour and 3 volumes of chlorine condensed into 2 volumes, the specific gravity of its vapour being 6.3.

Arsenious bromide much resembles the chloride in its chemical characters, but is a solid crystalline substance, easily fusible.

176. *Arsenic tri-iodide*, or *arsenious iodide* (AsI_3), is remarkable for not being decomposed by water, like the corresponding phosphorus compound. When obtained by heating arsenic and iodine together, it sublimes in brick-red flakes, which, if prepared on a large scale, hang in long laminæ, like sea-weed. It may be dissolved in boiling water, and crystallises out unchanged. It may even be prepared by heating 3 parts of arsenic with 10 of iodine and 100 of water, when the solution deposits red crystals of the hydrated tri-iodide, from which the water may be expelled by a gentle heat.

AsI_3 is precipitated as a golden crystalline powder on mixing a hot solution of As_2O_3 in HCl with a strong solution of KI.

Arsenic di-iodide, AsI_2, is obtained by heating 1 part of arsenic and 2 parts of iodine in a sealed tube to 230° C., and crystallising from CS_2 in an atmosphere of CO_2. It forms red prismatic crystals which become black when treated with water, according to the equation $3AsI_2 = 2AsI_3 + As$.

When iodine is dissolved in a hot solution of arsenious acid, this is oxidised to arsenic acid; $H_3AsO_3 + H_2O + I_2 = H_3AsO_4 + 2HI$. When the solution is concentrated by evaporation, the change is reversed, and iodine liberated.

The *arsenic tri-fluoride* (AsF_3) resembles the trichloride, but is much more volatile. It may be obtained by distilling 4 parts of arsenious oxide with 5 of fluor spar and 10 of strong sulphuric acid, in a leaden retort (see p. 180). It does not attack glass unless water be present, which decomposes it into arsenious and hydrofluoric acids. PCl_5 converts it into PF_5 and $AsCl_3$.

177. SULPHIDES OF ARSENIC.—There are three well-known sulphides of arsenic, having the composition As_2S_2, As_2S_3, and As_2S_5, the two former being found in nature.

Realgar (As_2S_2) is a beautiful mineral, crystallised in orange-red prisms; but the *red orpiment* used in the arts is generally prepared by heating a mixture of white arsenic and sulphur, when sulphurous acid gas escapes, and an orange-coloured mass of realgar is left—

$$2As_2O_3 + S_7 = 2As_2S_2 + 3SO_2.$$

Another process for preparing it consists in distilling arsenical pyrites with sulphur or with iron pyrites; $FeS_2.FeAs_2 + 2FeS_2 = 4FeS + As_2S_2$. The realgar distils over, and condenses to a red transparent solid. Realgar burns in air with a blue flame, yielding arsenious and sulphurous oxides. If it be thrown into melted saltpetre, it burns with a brilliant white flame, being converted into arsenate and sulphate of potassium. This brilliant flame renders realgar an important ingredient in *Indian fire* and similar compositions for fire-works and signal lights. A mixture of one part of red orpiment with 3.5 parts of sublimed sulphur and 14 parts of nitre is used for signal-light composition.

Realgar is not easily attacked by acids; nitric acid, however, dissolves it, with the aid of heat, forming arsenic acid and sulphuric acid, with separation of part of the sulphur in the free state. Alkalies (potash, for example) partly dissolve it, leaving a dark brown substance, which appears to contain free arsenic—

$$3As_2S_2 = 2As_2S_3 + As_2.$$

When exposed to air, realgar is partly oxidised and converted into a mixture of As_2S_3 and As_2O_3.

Yellow orpiment, or *arsenious sulphide* (As_2S_3), is found native in yellow prismatic crystals. The paint known as *King's yellow* is a mixture of arsenious sulphide and arsenious anhydride, prepared by subliming a mixture of sulphur with white arsenic; $S_9 + 2As_2O_3 = 2As_2S_3 + 3SO_2$. It is, of course, very poisonous.

This substance, like realgar, is not much affected by acids, excepting nitric acid;

but it dissolves entirely in potash, forming potassium arsenite and *sulpharsenite;* $6KHO + As_2S_3 = K_3AsS_3 + K_3AsO_3 + 3H_2O$. Ammonia also dissolves it easily, forming a colourless solution which is employed for dyeing yellow, since if a piece of stuff be dipped into it and exposed to air, the ammonia will volatilise, leaving the yellow orpiment behind. When As_2S_3 is boiled with a strong solution of sodium carbonate, H_2S is evolved and As_2S_2 is deposited as a crystalline powder.

The formation of the characteristic yellow sulphide is turned to account in testing for arsenic; if a solution prepared by boiling white arsenic with distilled water be mixed with a solution of hydrosulphuric acid, a bright yellow liquid is produced, which looks opaque by reflected, but transparent by transmitted, light, and may be passed through a filter without leaving any solid matter behind. This solution probably contains a soluble *colloidal* form of arsenious sulphide; it is, however, rendered insoluble by evaporation. The addition of a little hydrochloric acid, or of sal-ammoniac, and many other neutral salts will also cause a separation of the sulphide from this solution; even the addition of hard water will have that effect. If the solution of arsenious acid be acidified with hydrochloric acid before adding the hydrosulphuric acid, the bright yellow sulphide is precipitated at once, and may be distinguished from any other similar precipitate by its ready solubility in solution of ammonium carbonate.

Arsenic sulphide (As_2S_5) possesses far less practical importance than the preceding sulphides; it may be obtained by fusing As_2S_3 with sulphur, when it forms an orange-coloured glass, easily fusible, and capable of being sublimed without change. When hydrosulphuric acid gas is passed through solution of arsenic acid, a white precipitate of sulphur is first obtained, the hydrogen reducing the arsenic acid to arsenious acid; $H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$; and if the passage of the gas be continued, the arsenious acid is decomposed, and arsenious sulphide is precipitated; these changes are much accelerated by heat. But if a solution of sodium arsenate be saturated with hydrosulphuric acid, it is converted into sodium sulpharsenate. On adding hydrochloric acid to this solution, a bright yellow precipitate of arsenic sulphide is obtained.

Cuprous sulpharsenate, or *Clarite* (Cu_3AsS_4), is found in the Black Forest.

Arsenic phosphide, As_2P, is obtained by fusing phosphorus under solution of arsenious acid and treating the black mass with carbon disulphide, which dissolves the unaltered phosphorus and leaves a shining black powder. The presence of this body in phosphorus caused the mistaken belief in the existence of a black variety of phosphorus.

GENERAL REVIEW OF THE NON-METALLIC ELEMENTS.

178. At the conclusion of the history of the non-metals, it may be well to call attention to the points of resemblance which classify them into separate groups or families, most of which are connected, by some analogies, with one or more members of the class of metals.

Hydrogen stands alone among the non-metals, its chemical properties and functions being widely different from those of any other non-metal, but connecting it very closely with the most highly electro-positive (or *basylous*) metals, such as potassium and sodium.

Oxygen, *Sulphur*, *Selenium*, and *Tellurium* compose a group the members of which (in the state of vapour) combine with twice their volume of hydrogen to form compounds which (in the state of vapour) occupy the same volume as the hydrogen occupied before combination. All these hydrogen-compounds are capable of playing a feebly acid part, and their hydrogen may be displaced by an equivalent weight of a metal to produce compounds exhibiting a general agreement in chemical properties. This group is connected with the metals through tellurium, not only by its physical properties, but by its forming an oxide (TeO_2), which occasionally acts as a weak base.

Nitrogen, *Phosphorus*, and *Arsenic* are connected together by the general analogy of their hydrogen and oxygen compounds, the two last members of the group being far more closely connected with each other than with nitrogen. With the metals they are connected through arsenic, the hydrogen compound of which is very similar in properties, and probably in composition, to antimonetted hydrogen; arsenious oxide (As_2O_3) is also capable of occupying the place of antimonious oxide (Sb_2O_3) in certain salts of that oxide; and the sulphides of antimony correspond in composition, and in some of their properties, to those of arsenic. One form of arsenious oxide (the prismatic) is isomorphous with native oxide of antimony, and this oxide may be obtained in octahedra, the ordinary form of arsenious oxide, so that these oxides are *isodimorphous*.

These elements are also connected with the oxygen group through sulphur, selenium, and tellurium, the relations of which to hydrogen and the metals are somewhat similar to those of phosphorus and arsenic.

Carbon, *Boron*, and *Silicon* resemble each other in their allotropic forms, their resistance to fusion and volatilisation, and their forming feeble acids. To the metals they are allied through silicon, which resembles tin in the composition and character of its oxide and chloride.

This group is connected with the nitrogen group through boron, for boric acid resembles arsenious acid in its relations to bases, and in forming vitreous compounds with the alkalies. In certain compounds boric and arsenious oxides are interchangeable.

Chlorine, *Bromine*, *Iodine*, and *Fluorine* are intimately connected by numerous analogies, which have been already pointed out (p. 184). Some of the properties of iodine, as its relations to oxygen, and the solubility of its trichloride in water, connect it slightly with the metals, whilst some of the properties of the fluorides connect this group with the oxygen group of non-metallic elements.

ATOMICITY OR VALENCY—QUANTIVALENCE.

179. On examining the composition by volume of hydrochloric acid, water, ammonia, and marsh gas, it is seen that equal volumes of these compounds, measured in the gaseous state at the same temperature and pressure, contain respectively 1, 2, 3, and 4 volumes of hydrogen.

Thus 2 volumes of hydrochloric acid gas contain 1 volume of chlorine and 1 volume of hydrogen.
2 volumes of water vapour contain 1 volume of oxygen and 2 volumes of hydrogen.
2 volumes of ammonia contain 1 volume of nitrogen and 3 volumes of hydrogen.
2 volumes of marsh gas contain 1 volume (?) of imaginary carbon vapour and 4 volumes of hydrogen.

In the case of the marsh gas, it has been already explained that the volume occupied by a given weight of carbon vapour cannot be ascertained by experiment, but there are reasons to justify the assumption that 12 parts by weight of carbon vapour would occupy the same volume as 1 part by weight of hydrogen. In the other cases, the above statements exhibit the direct results of experiments previously described.

If it be allowed that one atom of each element occupies one volume, then hydrochloric acid, water, ammonia, and marsh gas will contain for one atom of chlorine, oxygen, nitrogen, and carbon, respectively, 1, 2, 3, and 4 atoms of hydrogen, or, taking the symbol for each element to represent one atom—

			Vols. H=1.	Weights. H=1.
Hydrochloric acid	= ClH	= HCl	= 2	= 36.5
Water	= OHH	= H_2O	= 2	= 18
Ammonia	= $NHHH$	= H_3N	= 2	= 17
Marsh gas	= $CHHHH$	= H_4C	= 2	= 16

Since, on the atomic theory, hydrogen is accepted as the unit of atomic weight and volume, it appears reasonable to fix upon it as representing the unit of combining power, and to classify the elements according to the tendency of their atoms to imitate the combining power of one or more atoms of hydrogen.

By the *atomicity* or *valency* of an element is meant the number expressing the hydrogen-atoms to which one atom (or volume) of that element is usually equivalent.

Since hydrochloric acid, water, ammonia, and marsh gas are the most conspicuous members of large classes of chemical compounds, they are often referred to as *types*, and the elements chlorine, oxygen, nitrogen, and carbon are taken as the representatives of the chief classes into which the elements are divided according to their combining powers or *valencies*.

One of the atoms of H in each of these typical molecules may be exchanged for another elementary atom, usually a metal; thus ClH gives $ClNa$; OH_2 gives $OH.Na$; NH_3 gives $NH_2.Na$; CH_4 gives $CH_3.Na$. It is evident that the groups OH, NH_2, and CH_3 are on the same footing as the elementary atom Cl in ClH, and they also resemble the elementary atom in being unable to exist in the separate state. Bodies of this kind are termed *radicals:* OH is the radical *hydroxyle*, NH_2 is the radical *amidogen*, CH_3 is the radical *methyle*. *A radical is a group capable of being exchanged for an element.*

Compounds formed upon the model of ClH, in which H is exchanged for a metal, are called *haloid salts;* such are ClK or KCl, KI. $(NH_4)Br$, &c. Evidently, if a diad, or triad, or tetrad metal is to be exchanged for the H, we must operate upon 2, 3, or 4 molecules of the ClH type. Thus upon the type $2HCl$ or H_2Cl_2, we have $CaCl_2$, $ZnCl_2$, $PbCl_2$. Upon the type $3HCl$ or H_3Cl_3 there are $SbCl_3$, $BiCl_3$. $AuCl_3$; and on the type $4HCl$ or H_4Cl_4, are $PtCl_4$ and $SnCl_4$. The Cl in any of these compounds may be replaced by Br, I, or F.

Compounds formed upon the model of OH_2 or $OH.H$, in which H is replaced by a metal, are called *hydrates;* for example, $OH.K$ or $K.HO$, $NaHO$, $NH_4.HO$. Here, again, we must take two or more molecules of the type for metals which are not monad; thus, on the type $2H_2O$ or $H_2(HO)_2$, we have $Ca(HO)_2$, $Zn(HO)_2$, $Pb(HO)_2$; on the type $3H_2O$ or $H_3(HO)_3$, there are $Sb(HO)_3$ and $Bi(HO)_3$; and on the type $4H_2O$ or $H_4(HO)_4$, $Pt(HO)_4$ and $Sn(HO)_4$.

When the whole of the H in the water has been exchanged for a metal, the compound is a *metallic oxide;* thus, on the type H_2O, are K_2O, Na_2O. Ag_2O, CaO, ZnO, PbO; on the type $2H_2O$ or H_4O_2, are PtO_2 and SnO_2; and on the type $3H_2O$ or H_6O_3, are Sb_2O_3 and Bi_2O_3.

When these metallic oxides are capable of exchanging atoms with HCl or bodies of the HCl type, so as to form corresponding chlorides, they are said to be *basic oxides* or *bases*. Thus, $Ag_2O + 2HCl = 2AgCl + H_2O$; $CaO + 2HCl = CaCl_2 + H_2O$; $Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O$; $PtO_2 + 4HCl = PtCl_4 + 2H_2O$. The following are the most important bases (inorganic):—K_2O, Na_2O, $(NH_4)_2O$?, Ag_2O, Hg_2O, Cu_2O, BaO, SrO, CaO, MgO, FeO, MnO, ZnO, CoO, NiO, HgO, CdO, CuO, PbO, SnO, Al_2O_3, Cr_2O_3, Fe_2O_3, Sb_2O_3, Bi_2O_3.

In this list it will be noticed that Hg, Cu, and Fe each forms two bases, viz., Hg_2O and HgO, Cu_2O and CuO, FeO and Fe_2O_3. Each of these forms corresponding chlorides and other haloid salts; Hg_2Cl_2 and $HgCl_2$, Cu_2Cl_2 and $CuCl_2$, $FeCl_2$ and Fe_2Cl_6; so that there would seem to be monad Hg and Cu in Hg_2O and Cu_2O, diad Hg and Cu in HgO and CuO; diad Fe in FeO and triad Fe in Fe_2O_3. In the cases of Hg and Cu, this may be explained by the union of single atoms of the diad metal to form a diad group; thus Hg would be diad in Cl—Hg—Cl, but would appear as if monad in Cl—Hg—Hg—Cl. In the case of Fe, the explanation is not so simple; it appears that there must be a diad form of the metal in Cl—Fe—Cl, and a tetrad form in $Cl_3 \equiv Fe—Fe \equiv Cl_3$, so that Fe_2 would be hexad.

In consequence of their disposition to form bases with oxygen, the metals are often spoken of as *basylous* radicals. They are also called *electro-positive* radicals because they are attracted to the negative pole of the battery. On the other hand, those elements which, like chlorine, form with the metals compounds of the NaCl type are called *chlorous* or *electro-negative* radicals.

The chief chlorous elements are F, Cl, Br, I, S, O.

The following elements are neither decidedly basylous nor decidedly chlorous, sometimes appearing in either aspect; As, B, C, N, P, Si.

The molecules of all the chlorous elements are capable of exchanging one of their atoms for hydrogen: thus FF forms HF, ClCl forms HCl, BrBr forms HBr, II forms HI, SS forms H_2S, OO forms H_2O. The compounds thus formed are able to exchange their H for a metal, thus forming the fluorides, chlorides, bromides, iodides, sulphides, and oxides, and, in the cases of H_2S and H_2O, the hydrosulphides, such as KHS, and the hydroxides or hydrates such as KHO.

Again, the H of molecules of the HCl type may be exchanged for a compound radical: thus, from the type HCl we get NO.Cl, nitrosyle chloride; $NO_2.Cl$, nitroxyle chloride; $PO_2.Cl$, metaphosphoryle chloride; $SbO_2.Cl$, antimonoxyle chloride. From the type H_2Cl_2 we have $SO_2.Cl_2$, sulphuryle chloride; $SO.Cl_2$, thionyle chloride; $CO.Cl_2$, carbonyle chloride; $CrO_2.Cl_2$, chromyle chloride; $SnO.Cl_2$, stannyle chloride. From H_3Cl_3 we get $PO.Cl_3$, phosphoryle chloride.

The chlorine in these compounds may be exchanged for hydroxyle, HO, when we obtain the corresponding *acids*—

Chlorides.	**Acids.**		**Chlorides.**	**Acids.**	
NO.Cl	NO.OH	nitrous	$CO.Cl_2$	$CO(OH)_2$	carbonic
$NO_2.Cl$	$NO_2.OH$	nitric	$SnO.Cl_2$	$SnO(OH)_2$	stannic
$PO_2.Cl$	$PO_2.OH$	metaphosphoric	PO.Cl	$PO(OH)_3$	orthophosphoric
$SbO_2.Cl$	$SbO_2.OH$	antimonic	BCl_3	$B(OH)_3$	boric
$SO.Cl_2$	$SO(OH)_2$	sulphurous	$AsCl_3$	$As(OH)_3$	arsenious
$SO_2.Cl_2$	$SO_2(OH)_2$	sulphuric	$SiCl_4$	$Si(OH)_4$	orthosilicic
$CrO_2.Cl_2$	$CrO_2(OH)_2$	chromic	CCl_4	$C(OH)_4$	orthocarbonic

The hydrogen contained in the hydroxyle present in these acids may be exchanged for a metal, forming a salt. Thus nitrous acid yields potassium nitrite, NO.OK; nitric acid gives the nitrate $NO_2.OK$; sulphurous acid gives potassium sulphite, $SO(OK)_2$; sulphuric acid, the sulphate $SO_2(OK)_2$; orthophosphoric acid gives potassium orthophosphate, $PO(OK)_3$; and orthosilicic acid, potassium orthosilicate, $Si(OK)_4$. Those acids which contain only one OH group are *monobasic;* two, *dibasic;* three, *tribasic;* four, *tetrabasic.*

Normal salts are those in which all the H of the hydroxyle is replaced by metal, as in the potassium salts mentioned above. *Acid salts* have only part of the H replaced by a metal, as in hydropotassium sulphite, SO.OH.OK; hydropotassium carbonate, CO.OH.OK; hydrodipotassium phosphate, $PO(OH)_2.OK$. *Basic salts* are generally composed of a normal salt and a hydrate of the metal, as in basic bismuth nitrate, $Bi(NO_3)_3.2Bi(OH)_3$; basic cupric carbonate, $CuCO_3.Cu(OH)_2$; and basic lead carbonate, $2PbCO_3.Pb(OH)_2$. *Double salts* are those in which the H of the hydroxyle has been exchanged for different metals, as in potassium-sodium carbonate, CO.OK.ONa; potassium-aluminium sulphate (alum), $(SO_2)_2.OK.O_3Al'''$.

Chemical equivalents.—The observation of the reciprocal action between acids and alkalies laid the foundation of quantitative chemistry. It was noticed that 112 grammes of KHO neutralised 98 grammes of sulphuric acid, 73 of hydrochloric, and 126 of nitric acid, so that these numbers were said to represent equivalent quantities of the three acids. Again, 98 grammes of H_2SO_4 were found to neutralise 112 grammes of caustic potash, 80 of caustic soda, and 74 of slaked lime, so that 112 of potash are equivalent to 80 of soda and to 74 of slaked lime. From experiments of this kind, Tables of Equivalents were constructed, in order to show, at a glance, how much of any alkaline body must be used to neutralise a given quantity of any acid body, or the reverse, thus—

Alkaline.		**Acid.**	
Potash	112	Sulphuric	98
Soda	80	Hydrochloric	73
Lime	74	Nitric	126

By means of a slide rule containing the equivalent numbers, calculation is often saved.

CHEMISTRY OF THE METALS.

180. The definition of a metal has been already given at page 31, as *an element capable of forming a base by union with oxygen.* It will also be noticed that the metals are but little disposed to form combinations with hydrogen; but that they evince very powerful attraction for the chlorine group of elements, with which they form, as a rule, compounds which dissolve, without apparent decomposition, in water.

CLASSIFICATION OF THE METALS.

The metals may be divided into ten classes or groups.

I. *Potassium group.*—The metals of this group are distinguished by their property of forming hydrates which are very soluble in water and very strongly alkaline. Each metal of this group forms one chloride, containing one atom of metal and one atom of chlorine. They take up oxygen at once from the air, and their chemical energies increase with their atomic weights. Their salts are very stable, and are almost all soluble in water.

	Atomic Weight.		Atomic Weight.
Lithium	7	Rubidium	85.3
Sodium	23	Cæsium	133
Potassium	39.1		

This group is linked to the next by lithium, which forms a sparingly soluble carbonate and phosphate.

II. *Calcium group.*—The metals of this group form hydrates which are much less soluble in water than those of the potassium group, but which are also strongly alkaline. Each metal of this group forms a chloride containing one atom of the metal and two atoms of chlorine.

The sulphates of the metals of this group are nearly insoluble in water. The chemical energies of these metals also increase with their atomic weights.

	Atomic Weight.
Calcium	40
Strontium	87.5
Barium	137

III. *Magnesium group.*—The metals of this group also form one chloride, containing one atom of metal and two atoms of chlorine; but they form hydrates which are not soluble in water, and are not strongly alkaline. These metals decompose hydrochloric acid very readily. Their chemical energies decrease with the rise in the atomic weight.

	Atomic Weight		Atomic Weight.
Glucinum	9.2	Zinc	65.5
Magnesium	24.3	Cadmium	112.3

In the cases of zinc and cadmium it has been proved that the atomic weight of the metal occupies two volumes in the state of vapour, so that the molecular weight is the same as the atomic weight, and it is believed that this is also the case with beryllium (or glucinum) and magnesium.

IV. *Aluminium group.*—The metals of this group are dissolved by HCl, forming chlorides containing two atoms of metal and six atoms of chlorine. Each metal also forms one oxide, which is a weak base, and contains two atoms of the metal and three atoms of oxygen. Their hydrates form gelatinous precipitates, which are soluble either in alkalies or in their carbonates. Their sulphates form *alums* with the sulphates of monad metals. The metals enclosed in parentheses have been but little studied, and it is doubtful whether their chlorides and oxides are composed as above stated, though their general characters appear to give them a place in this group.

	Atomic Weight.		Atomic Weight.
Aluminium	27	Indium	113.4
(Yttrium	89.8)	Lanthanium	139
Gallium	68.8	Didymium	144.8
(Zirconium	90)	(Thorium	232)
(Erbium	165.9)		

V. *Iron group.*—The metals of this group are capable of forming compounds of two classes in which the metals are, respectively, diad and triad; they also form two compounds with oxygen, one of which contains single atoms of the metal and oxygen, and is a pretty strong base; the other contains two atoms of metal combined with three atoms of oxygen, and behaves to acids either as a weak base or as an indifferent oxide. (Cerium will be found to present an exception in the composition of its oxides.) The metals dissolve in HCl, forming dichlorides. Their compounds (excepting those of cerium) are remarkable for their strong colours.

	Atomic Weight.		Atomic Weight.
Iron	56	Uranium	120
Cobalt	59	(Cerium	140.5)
Nickel	59		

VI. *Manganese group.*—The metals of this group differ from those of the preceding groups by forming well-defined salts in which the metal enters into the composition of the acid radical (viz., chromates, manganates, vanadates, molybdates). From the groups which follow, this group is distinguished by forming at least two chlorides, containing metal and chlorine in the atomic ratios of 1 : 2 and 1 : 3 respectively. Some of their compounds are remarkable for their strong colours.

	Atomic Weight.		Atomic Weight.
Vanadium	51.3	Manganese	55
Chromium	52.5	Molybdenum	96

VII. *Antimony group.*—The two members of this group are brittle metals, the chlorides of which are easily decomposed by water.

	Atomic Weight.
Antimony	120
Bismuth	208

VIII. *Tin group.*—Each of the metals of this group forms a compound with two* atoms of oxygen which is insoluble in acids but dissolves in the alkalies, forming salts.

	Atomic Weight.		Atomic Weight.
Titanium	48	Tantalum	182
Niobium	94	Tungsten	184
Tin	118		

Titanium and tin are very closely related to silicon.

IX. *Silver group.*—The metals of this group are capable of forming an insoluble chloride.

	Atomic Weight.		Atomic Weight.
Copper	63.5	Thallium	204
Silver	108	Lead	207
Mercury	200		

X. *Platinum group.*—The metals of this group form chlorides which combine with the chlorides of the metals of Group I. to form easily crystallised double salts. These metals are all rare and costly.

	Atomic Weight.		Atomic Weight.
Rhodium	104.3	Platinum	197.1
Ruthenium	104.2	Iridium	192.5
Palladium	105.7	Osmium	200
Gold	196.8		

Periodic law of the chemical elements (*Newlands' and Mendelejeff's law*).—When there is a great resemblance between the members of a group of elements, there is generally a certain regularity in the increase of their atomic weights, so that each group shows indications of an arithmetical progression.

If a list of the elements be drawn up in the order of their atomic weights, the first seven (after hydrogen) will be found to be representative of different groups; thus, lithium (at. wt. 7) represents the group which forms oxides of the formula R_2O; glucinum or beryllium (at. wt. 9) represents the group forming oxides of the formula RO; boron (at. wt. 11), the group forming the oxides R_2O_3; carbon (at. wt. 12), the group which forms oxides of the formula RO_2; nitrogen (at. wt. 14) represents the group forming oxides R_2O_3 and hydrides RH_3; oxygen (at. wt. 16), the group forming oxides RO_3 and hydrides RH_2; and fluorine (at. wt. 19), the group forming oxides R_2O_7 and hydrides RH.

Let each of these seven elements head a column, and arrange the rest of the elements under them in the order of their atomic weights. They will be found to approximate to a series with periodically recurring changes in the chemical and physical functions of its members.

By observing the gaps which exist in this series, Mendelejeff endeavours to predict the properties of elements which have yet to be discovered, and did indeed foretell, with considerable precision, the properties of gallium, in anticipation of its discovery.

The following table illustrates this periodic law; the elements being divided into 7 groups according to the formulæ of their oxides or hydrides, as given at the head of each column, and into 7 series, in the order of their increasing atomic weights:—

* Except in the case of tungsten.

Group	1	2	3	4	5	6	7
Series.	R_2O	RO	R_2O_3	RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7
1	Li 7	G 9	B 11	C 12	N 14	O 16	F 19
2	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35
3	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55
4	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 78	Br 80
5	Rb 85	Sr ·87	Y 89	Zr 90	Nb 94	Mo 96	...
6	Ag 108	Cd 112	In 113	Sn 118	Sb 122	Te 128	I 127
7	Cs 133	Ba 137	La 139	Ce 141	Di 145	Sm	...

The blanks in such a table indicate where new elements may be expected. Thus, the 5th member of group 7 is as yet unknown, and its properties must be similar to those of bromine and iodine.

This periodic classification of the elements bears some resemblance to the classification of organic compounds in homologous series.

POTASSIUM.

$K' = 39.1$ parts by weight.

181. Potassium is found in abundance, as potassium chloride, in certain salt-mines (see below), and it is contained in granite, of which it forms about 5 or 6 per cent. The indispensable alkali, *potash*, appears to have been originally derived from the granitic rocks, where it exists, in combination with silica and alumina, in the well-known minerals *felspar* and *mica*. These rocks having, in course of time, disintegrated to form soils for the support of plants, the potash has been converted into a soluble state, and has passed into the plants as a necessary portion of their food.

In the plant, the potash is found to have entered into various forms of combination; thus, most plants contain sulphate and chloride of potassium; but the greater portion of the potassium exists in the form of salts of certain vegetable acids formed in the plant, and when the latter is burnt, these salts are decomposed by the heat, leaving the potassium in the form of carbonate.

Potassium carbonate, or *carbonate of potash*, K_2CO_3.—When the ashes of plants are treated with water, the salts of potassium are dissolved, those of calcium and magnesium being left. On separating the aqueous solution and evaporating it to a certain point, a great deal of the potassium sulphate, being much less soluble, is deposited, and the carbonate remains in the solution; this is evaporated to dryness, when the carbonate is left, mixed with much potassium chloride, and some sulphate; this mixture constitutes the substances imported from America and other countries where wood is abundant, under the name of *potashes*, which are much in demand for the manufacture of soap and glass. When further purified, these are sold under the name of *pearlash*, but this is still far from being pure potassium carbonate.

During the fermentation of the grape-juice, in the preparation of wine, a hard crystalline substance is deposited, which is known in commerce by the name of *argol*, or, when purified, as *cream of tartar*. The chemical name of this salt is bitartrate of potash or hydropotassium tartrate, for it is derived from potash and tartaric acid, a vegetable acid having the composition $H_2C_4H_4O_6$. When this salt ($KHC_4H_4O_6$) is heated, it leaves potassium carbonate mixed with carbon; but if the heat be continued, and free access of air permitted, the carbon will be entirely burnt away, and potassium carbonate will be left (*salt of tartar*).

In wine-producing countries potassium carbonate is prepared from the refuse yeast which rises during the fermentation, and is dried in the sun in order to be subsequently incinerated.

The fleeces of sheep contain a considerable proportion of a salt of potassium with an animal acid; when the fleece is washed with water, this salt is dissolved out, and on evaporating the liquid and burning the residue it is converted into potassium carbonate.

Potassium carbonate is also made from potassium sulphate by a process similar to that by which sodium sulphate is converted into carbonate (183). Potassium chloride is converted into potassium carbonate by decomposing it with the carbonate of trimethylamine (see *Trimethylamine*).

Potassium carbonate is deliquescent and very soluble in water, yielding a strongly alkaline solution. It may be crystallised in prisms of the formula $2K_2CO_3.3H_2O$, which become $K_2CO_3.H_2O$ at 100° C. It is insoluble in alcohol.

Bicarbonate of potash or *hydropotassium carbonate*, $KHCO_3$, often sold as the carbonate and used in medicine, is made by saturating moist K_2CO_3 with CO_2, or by passing CO_2 through a strong solution of K_2CO_3 (in three parts of water). It forms prismatic crystals which are much less alkaline and less soluble in water (30.4 per cent. at 15° C.) than the normal carbonate, into which they are converted by heat; $2KHCO_3 = K_2CO_3 + H_2O + CO_2$. The aqueous solution of $KHCO_3$ gradually loses CO_2 when boiled.

Hydrate of potash, or *potassium hydrate*, KHO.—Potassium carbonate was formerly called potash, and was supposed to be an elementary substance. It was known that its alkaline qualities were rendered far more powerful by treating it with lime, which caused it to be termed *mild* alkali, in order to distinguish it from the *caustic*[*] alkali obtained by means of lime, and possessed of very powerful corrosive properties. Lime, it was said, is derived from limestone by the action of fire, and therefore owes its peculiar properties to the acquisition of a certain amount of the matter of fire, which, in turn, it imparts to the mild alkali, and thus confers upon it a caustic or burning power.

Black's researches in the middle of the eighteenth century, which are often referred to as models of inductive reasoning, exposed the fallacy of this explanation, and proved that instead of acquiring anything from the fire, the limestone actually lost carbonic acid gas, and instead of imparting anything to the mild alkali, the lime really gained as much carbonic acid as it previously lost.

The caustic potash, so largely employed by the soap-maker, is obtained by adding slaked lime to a boiling diluted solution of the potassium carbonate, when calcium carbonate is deposited at the bottom of the vessel, whilst *potassium hydrate* remains in the clear solution—

$$\underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Calcium}\\ \text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Potassium}\\ \text{hydrate.}}}{2KHO}$$

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[*] From καίω, to burn.

If the solution be too strong, the lime will not decompose the carbonate.

When the solution is evaporated, the potassium hydrate remains as a clear oily liquid, which solidifies to a white mass as it cools, and forms the fused potash of commerce, which is often cast into cylindrical sticks for more convenient use.* Potassium hydrate is vaporised at high temperatures without decomposition. It readily absorbs water and CO_2 from the air. Half its weight of water suffices to dissolve it, with great evolution of heat. A strong solution deposits crystals of $KHO.2Aq$. Alcohol dissolves it easily. In the laboratory, KHO is prepared by dissolving 1 lb. (or 500 grms.) of K_2CO_3 in a gallon (or 5 litres) of distilled water, boiling the solution in a clean iron or nickel pan, and gradually stirring in 12 oz. (or 380 grms.) of slaked lime mixed with water to a thin cream. After boiling and stirring for ten minutes, the vessel is covered and allowed to cool, when the $CaCO_3$ will have subsided, and the clear liquid may be drawn off with a siphon, and boiled down in an iron or nickel or silver basin till all ebullition ceases, and an oily liquid remains which solidifies on cooling. The potassium hydrate is the most powerful alkaline substance in ordinary use, and is very frequently employed by the chemist. It is generally used in the state of solution, the strength of which is inferred from its specific gravity, which increases with the amount of potash contained in the solution.

Potassium.—Of the composition of potassium hydrate nothing was known till the year 1807, when Davy succeeded in decomposing it by the galvanic battery; this experiment, which deserves particular notice, as being the first of a series resulting in the discovery of so many important metals, was made in the following manner:—A fragment of potassium hydrate, which, in its dry state, does not conduct electricity, was allowed to become slightly moist by exposure to the air, and placed upon a plate of platinum attached to the copper end of a very powerful galvanic battery; when the wire connected with the zinc end was made to touch the surface of the hydrate, some small metallic globules resembling mercury made their appearance at the extremity of this (negative) wire, at which the hydrogen contained in the hydrate was also eliminated, whilst bubbles of oxygen were separated on the surface of the platinum plate connected with the positive wire (see p. 11). By allowing the negative wire to dip into a little mercury contained in a cavity upon the surface of the potash, a combination of potassium with mercury was obtained, and the mercury was afterwards separated by distillation. This process, however, furnished the metal in very small quantities, and, though it was obtained with greater facility a year or two afterwards by decomposing potassium hydrate with white-hot iron, some years elapsed before any considerable quantity of potassium was prepared by the present method of distilling in an iron retort an intimate mixture of potassium carbonate and carbon, obtained by calcining cream of tartar; in this process the oxygen of the carbonate is removed by the carbon in the form of carbonic oxide ($K_2CO_3 + C_2 = K_2 + 3CO$).

Fig. 223 represents the iron retort connected with its copper receiver, surrounded with cold water, and containing petroleum to protect the distilled potassium from oxidation. The lateral tube of the receiver permits the tube of the retort to be cleared, if necessary, during the distillation, by the passage of an iron rod.

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* These have sometimes a greenish colour, due to the presence of some potassium manganate.

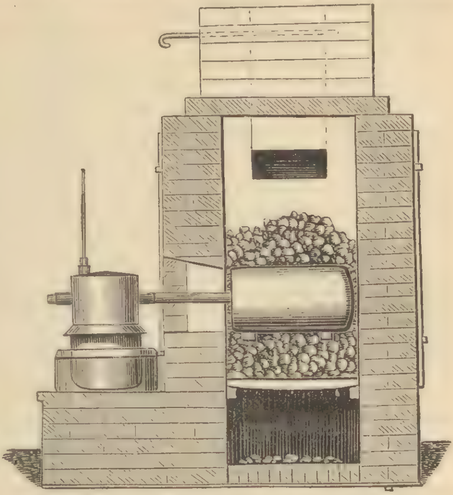

Fig. 223.—Preparation of potassium.

Some of the most striking properties of this metal have already been referred to (p. 13); its softness, causing it to be easily cut like wax, the rapidity with which its silvery surface tarnishes when exposed to the air, its great lightness (sp. gr. 0.865), causing it to float upon water, and its taking fire when in contact with that liquid, sufficiently distinguish it from other metals. It fuses at 62°.5 C. and boils at a low red heat, yielding a green vapour; if air be present, it burns with a violet-coloured flame, and is converted into *anhydrous potash*, or di-potassium oxide (K_2O).

The property of burning with this peculiar violet-coloured flame is characteristic of potassium, and allows it to be recognised in its compounds.

If a solution of potassium nitrate (saltpetre) in water be mixed with enough spirit of wine to allow of its being inflamed, the flame will have a peculiar lilac colour. This colour may also be developed by exposing a very minute particle of saltpetre, taken on the end of a heated platinum wire, to the reducing (inner) blowpipe flame (fig. 224), when the potassium, being reduced to the metallic state and passing into the oxidising (outer) flame in the state of vapour, imparts to that flame a lilac tinge.

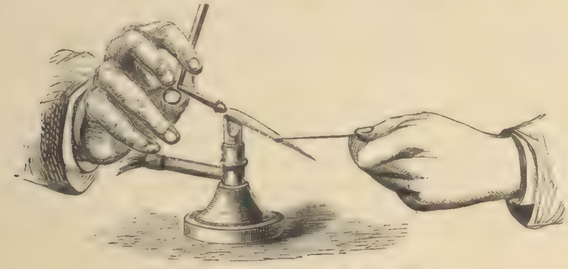

Fig. 224.—Coloured flame test.

The difficulty and expense attending the preparation of potassium have prevented its receiving any application except in purely chemical operations, where its attraction for oxygen, chlorine, and other electro-negative elements is often turned to account.

Potassium hydride, K_2H, is formed when potassium is heated in hydrogen to about 350° C. It forms a silvery brittle mass, which takes fire in air and is decomposed in a vacuum at 200° C.

Di-potassium oxide, K_2O, is formed when KHO is heated with potassium, hydrogen being expelled.

Di-potassium tetroxide, K_2O_4, is a yellow powder formed when potassium is heated in oxygen.

Di-potassium dioxide, corresponding to hydric peroxide, is formed when K_2O_4 is dissolved in water, oxygen being disengaged. This oxide appears to be the source of the bubbles of oxygen sometimes evolved when the commercial potassium hydrate is dissolved in water.

Potassium chloride (KCl) is an important natural source of this metal, being extracted from sea water, from kelp (the ash of sea-weed), and from the refuse of the manufacture of sugar from beet-root. It also occurs in combination with magnesium chloride, forming the mineral known as *carnallite* ($KCl.MgCl_2.6H_2O$), an immense saline deposit overlying the rock-salt in the salt-mines of Stassfurt, in Saxony. Carnallite resembles rock-salt in appearance, but is very deliquescent; it promises to become the most important source of potassium hitherto discovered. Considerable deposits containing chloride and sulphate of potassium have also been found in East Galicia. Potassium chloride crystallises in cubes; it is very soluble in water and insoluble in alcohol.

Potassium chlorate, $KClO_3$, is prepared as described at page 162. It crystallises in four-sided tables, which dissolve in 16 parts of cold and 2 parts of boiling water. It fuses at 334° C., and is decomposed at 352°, when it gives off oxygen, and leaves, at first, a mixture of chloride and perchlorate, and lastly chloride only; $2KClO_3 = KClO_4 + KCl + O_2$. Its action on combustible bodies and consequent useful applications have been described at page 163.

Potassium perchlorate, $KClO_4$, is remarkable for its sparing solubility, for it requires 70 parts of cold water to dissolve it. It is prepared by heating $KClO_3$ until 12 grammes have evolved a litre of oxygen, as shown in the above equation; the mass is boiled with just enough water to dissolve it, and the solution, on cooling, deposits crystals of $KClO_4$, leaving the KCl in solution. The perchlorate is decomposed at 400° C. into KCl and O_4.

Potassium bromide, KBr, forms cubical crystals very soluble in water.

Potassium iodide, KI, is prepared by adding iodine in small quantities to solution of potash till it is coloured slightly brown, when a mixture of potassium iodide and iodate is obtained; $6KHO + I_6 = KIO_3 + 5KI + 3H_2O$. The solution is evaporated to dryness, the residue mixed with one-tenth of its weight of powdered charcoal, thrown in small quantities into a red-hot iron crucible and fused; $KIO_3 + C_3 = KI + 3CO$. The fused mass is dissolved in hot water, filtered, evaporated till a film appears upon the surface, and set aside to crystallise.

Potassium iodide forms cubical crystals very soluble in water, but sparingly soluble in alcohol. It is of the greatest importance in medicine, in chemical analysis, and in photography.

Potassium tri-iodide, KI_3, obtained by saturating potassium iodide with iodine and evaporating over sulphuric acid, forms dark brown needles with a metallic lustre, very deliquescent, and easily decomposed into KI and I_2.

Potassium iodate, KIO_3, is useful in testing for SO_2, and may be prepared for that purpose by mixing 50 grains of iodine with an equal weight of potassium chlorate in fine powder, adding, in a flask, about half a measured ounce of nitric acid, and digesting till the colour disappears. The liquid is then boiled for a minute, poured into a dish, evaporated to dryness, and moderately heated, when it leaves a mixture of potassium iodate and a little potassium chloride which may be dissolved in water. SO_2 at once liberates iodine from it, which gives a blue colour to starch.

Potassium fluoride, KF, is prepared by neutralising HF with K_2CO_3. Crystallised by slow evaporation of a cold solution, it gives $KF.2H_2O$, but above 35° C. it yields cubes of KF. It is deliquescent and easily soluble; the solution corrodes glass. It combines with HF, forming KF.HF, which is employed for the preparation of pure HF.

Sulphides of potassium, K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, K_2S_7.

Di-potassium sulphide, K_2S, is obtained as a red crystalline mass by heating K_2SO_4 in hydrogen. It exists in the residue left by the explosion of gunpowder. Water decomposes it, so that it smells of H_2S when exposed to moist air.

Solution of K_2S is prepared by saturating solution of KHO with H_2S, and adding another equal quantity of KHO. In the first operation KHS is formed, which is converted into K_2S on adding KHO. From the solution, crystals of $K_2S.5H_2O$ may be obtained.

Potassium hydrosulphide, KHS, may be formed by displacing half the H in H_2S by K, or by heating K_2CO_3 to redness in H_2S; $K_2CO_3 + 2H_2S = 2KHS + H_2O + CO_2$. It is a yellow solid, very soluble in water, and crystallising as $2KHS.H_2O$. When exposed to air, the solution becomes yellow, from the formation of di-potassium disulphide; $2KHS + O = K_2S_2 + H_2O$. On longer exposure, the solution becomes colourless, potassium thiosulphate being formed; $K_2S_2 + O_3 = K_2S_2O_3$.

Potassium sulphate, K_2SO_4, is found in certain salt-mines, in the mineral *Kainite*, $K_2SO_4.MgSO_4.MgCl_2.6Aq$. This is decomposed by boiling water, and the K_2SO_4 crystallises on cooling in rhombic prisms which are rather sparingly soluble in cold water (10 parts), but easily in boiling water (4 parts). It is also obtained as a by-product in some chemical manufactures, and is used in making alum.

Bisulphate of potash, or *hydropotassium sulphate*, $KHSO_4$, is obtained as the residue in the preparation of nitric acid from saltpetre. It is more fusible and more soluble in water than the normal sulphate. Its solution is strongly acid. Much water decomposes it into sulphuric acid and K_2SO_4. When heated, it undergoes decomposition in two stages; (1) $2KHSO_4 = H_2O + K_2S_2O_7$ (*pyrosulphate*); (2) $K_2S_2O_7 = K_2SO_4 + SO_3$.

The bisulphate is very useful in chemical operations for decomposing minerals at high temperatures, its hydrogen easily giving place to metals.

Potassium nitrate (KNO_3), or *saltpetre*, will be specially considered in the section on gunpowder.

It is found in the soil of India and other hot climates in the dry season, and is also made by decomposing sodium nitrate with potassium chloride. It forms characteristic six-sided prismatic crystals which fuse at 339° C., and are decomposed at a strong red heat, leaving, first, potassium nitrite, KNO_2, and at last K_2O mixed with K_2O_2. The fused salt attacks all oxidisable bodies, and the K_2O attacks siliceous bodies, so that it is difficult to find a vessel capable of resisting it at a high temperature. Platinum gives way, but gold is less corroded. Nitre is soluble in four times its weight of cold water and in one-third of its weight of hot water. It is insoluble in alcohol.

SODIUM.

$Na' = 23$ parts by weight.

182. Sodium is often found, in place of potassium, in the felspars and other minerals, but we are far more abundantly supplied with it in the form of *common salt* (sodium chloride, NaCl), occurring not only in the solid state, but dissolved in sea water, and in smaller quantity in the waters derived from most lakes, rivers, and springs.

Rock-salt forms very considerable deposits in many regions; in this country the most important is situated at Northwich, in Cheshire, where very large quantities are extracted by mining. Wielitzka, in Poland, is celebrated for an extensive salt-mine, in which there are a chapel and dwelling-rooms, the furniture of which is made of this rock. Extensive beds of rock-salt also occur in France, Germany, Hungary, Spain, Abyssinia, and Mexico. Perfectly pure specimens form beautiful colourless cubes, and are styled *sal gemme;* but ordinary rock-salt is only partially transparent, and exhibits a rusty colour, due to the presence of iron. In some places the salt is extracted by boring a hole into the rock and filling it with water, which is pumped up when saturated with salt, and evaporated in boilers, the minute crystals of salt being removed as they are deposited.

At Droitwich, in Worcestershire, the salt is obtained by evaporation from the waters of certain salt springs. In some parts of France and Germany the water from the salt springs contains so little salt that it would not pay for the fuel necessary to evaporate the water, and a very ingenious plan is adopted by which the proportion of water is greatly reduced without the application of artificial heat. For this purpose a lofty scaffolding is erected and filled with bundles of brushwood, over which the salt water is allowed to flow, having been raised to the top of the scaffolding by pumps. In trickling over the brushwood this water exposes a large surface to the action of the wind, and a considerable evaporation takes place, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation, the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat. The brine is run into boilers and rapidly boiled for about thirty hours, fresh brine being allowed to flow in continually, so as to maintain the liquid at the same level in the boiler. During this ebullition a considerable deposit, composed of the sulphates of calcium and sodium, is formed, and raked out by the workmen. When a film of crystals of salt begins to form upon the surface, the fire is lowered, and the temperature of the brine allowed to fall to about 180° F., at which temperature it is maintained for several days whilst the salt is crystallising. The crystals are afterwards drained and dried by exposure to air. The grain of the salt is regulated by the temperature at which it crystallises, the size of the crystals increasing as the temperature falls. It is not possible to extract the whole of the salt in this way, since the last portions which crystallise will always be contaminated with other salts present in the brine; but the *mother-liquor* is not wasted, for after as much salt as possible has been obtained, it is made to yield sodium sulphate (Glauber's salt), magnesium sulphate (Epsom salts), bromine, and iodine.

The process adopted for extracting the salt from sea water depends upon the climate. In Russia, shallow pits are dug upon the shore, in which the sea water is allowed to freeze, when a great portion of the water separates in the form of pure ice, leaving a solution of salt sufficiently strong to pay for evaporation.

Where the climate is sufficiently warm, the sea water is allowed to run very slowly through a series of shallow pits upon the shore, where it becomes concentrated by spontaneous evaporation, and is afterwards allowed to remain for some time in reservoirs in which the salt is deposited. The coarse crystals thus obtained are known in commerce as *bay-salt*. Before they are sent into the market they are allowed to drain for a long time, in a sheltered situation, when the magnesium chloride with which they are contaminated deliquesces in the moisture of the air and drains off. The *bittern*, or liquor remaining after the salt has been extracted, is employed to furnish magnesia and bromine.

1000 parts of sea water contain about 29 parts of sodium chloride, 0.5 of potassium chloride, 3 of magnesium chloride, 2.5 of magnesium sulphate, 1.5 of calcium sulphate, &c.

In a warm climate, that of Marseilles, for example, the water is allowed to evaporate spontaneously until it has a specific gravity of 1.24. During this evaporation it deposits about four-fifths of its sodium chloride. It is then mixed with one-tenth of its volume of water, and artificially cooled to 0° F. (see p. 127), when it deposits a quantity of sodium sulphate, resulting from the decomposition of part of the remaining sodium chloride by the magnesium sulphate. The mother-liquor is evaporated down till its specific gravity is 1.33, a fresh quantity of sodium chloride being deposited during the evaporation. When the liquid cools, it deposits a double salt composed of chlorides of potassium and magnesium, from which the latter chloride may be extracted by washing with a very little water, leaving the potassium chloride fit for the market.

This process is instructive as illustrating the influence exerted upon the arrangement of the various acids and bases in a saline solution by the temperature to which the solution is exposed, the general rule being that the salt is formed which is least soluble in the liquid at the particular temperature.

The great tendency observed in ordinary table salt to become damp when exposed to the air, is due chiefly to the presence of small quantities of chlorides of magnesium and calcium, for pure sodium chloride has very much less disposition to attract atmospheric moisture, although it is very easily dissolved by water, $2\frac{3}{4}$ parts being able to dissolve 1 part (by weight) of salt.

The cubical crystals deposited on evaporation are anhydrous, but crystals of $NaCl.2Aq$ have been obtained in needles from a solution of salt in hot hydrochloric acid.

In the history of the useful applications of common salt is to be found one of the best illustrations of the influence of chemical research upon the development of the resources of a country, and a capital example of a manufacturing process not based, as such processes usually are, upon mere experience, independent of any knowledge of chemical principles, but upon a direct and intentional application of these to the attainment of a particular object.

Until the last quarter of the eighteenth century, the uses of common salt were limited to culinary and agricultural purposes, and to the glazing of the coarser kinds of earthenware, whilst a substance far more useful in the arts, *carbonate of soda*, was imported chiefly from Spain under the name of *barilla*, which was the ash obtained by burning a marine plant known as the *salsola soda*. But this ash only contained about one-fourth of its weight of carbonate of soda, so that this latter substance was thus imported at a great expense, and the manufactures of soap and glass, to which it is indispensable, were proportionally fettered.

During the wars of the French Revolution the price of barilla had risen so considerably, that it was deemed advisable by Napoleon to offer a premium for the discovery of a process by which the carbonate of soda could be manufactured at home, and to this circumstance we are indebted for the discovery, by Leblanc, of the process at present in use for the manufacture of carbonate of soda from common salt, a discovery which placed this substance at once among the most important raw materials with which a country could be furnished.

183. *Manufacture of carbonate of soda from common salt.*—The salt is spread upon the hearth of a *reverberatory* furnace (fig. 225),* and mixed with an equal weight of sulphuric acid, which converts it into sodium sulphate, expelling hydrochloric acid in the form of gas, which would prove highly injurious to the vegetation in the neighbourhood, and is therefore usually condensed by being brought into contact with water (see p. 156). The flame of the fire is allowed to play over the surface of the mixture of salt and sulphuric acid until it has become perfectly dry; in this state it is technically known as *salt cake*, and is next mixed with about an equal weight of limestone and rather more than half its weight of small coal; this mixture is again heated upon the hearth of a reverberatory furnace, when it evolves an abundance of carbonic oxide, and yields a mixture of sodium carbonate with lime and calcium sulphide; this mixture is technically known as *black ash*.

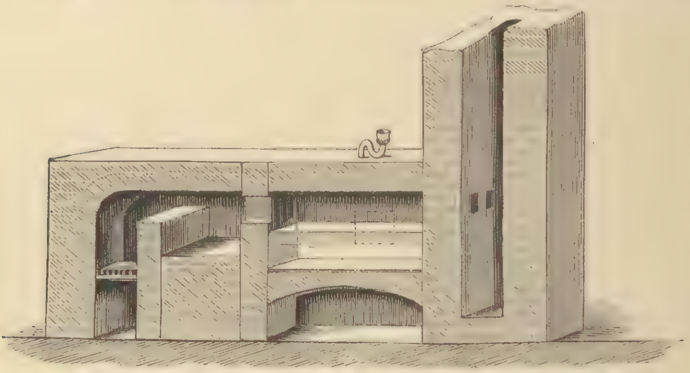

Fig. 225.—Furnace for converting common salt into sulphate of soda.

The change which has been effected in the sodium sulphate will be easily understood; for when this salt is heated in contact with carbon (from the small coal) it loses its oxygen, and becomes sodium sulphide, whilst carbonic oxide gas is evolved; thus, $Na_2SO_4 + C_4 = Na_2S + 4CO$. Again, when calcium carbonate is heated in contact with carbon, carbonic oxide is given off, and lime remains; $CaCO_3 + C = 2CO + CaO$. Finally, when sodium sulphide and lime are heated together in the presence of carbonic acid gas, sodium carbonate and calcium sulphide are produced; $Na_2S + CaO + CO_2 = Na_2CO_3 + CaS$.

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* The hearth of this furnace is usually divided, as seen in the figure, into two compartments, in one of which (lined with lead), more remote from the grate, the decomposition is effected, the acid being poured in through the funnel, while in that nearest to the grate, lined with firebrick, the whole of the hydrochloric acid is expelled, and the sodium sulphate fused.

When the black ash is treated with water, the sodium carbonate is dissolved, leaving the calcium sulphide, and by evaporating the solution, ordinary *soda ash* is obtained.* But this is by no means pure sodium carbonate, for it contains, in addition to a considerable quantity of common salt and sodium sulphate, a certain amount of caustic soda, formed by the action of the excess of lime upon the carbonate. In order to purify it, the crude soda ash is mixed with small coal or sawdust and again heated, when the carbonic acid gas formed from the carbonaceous matter converts the caustic soda into carbonate, and on dissolving the mass in water and evaporating the solution, it deposits oblique rhombic prisms of common washing soda, having the composition $Na_2CO_3.10Aq$ (*soda crystals*).

A little reflection will show the important influence which this process has exerted upon the progress of the useful arts in this country. The three raw materials, salt, coal, and limestone, we possess in abundance. The sulphuric acid, when the process was first introduced, bore a high price, but the resulting demand for this acid gave rise to so many improvements in its manufacture that its price has been very greatly diminished—a circumstance which has of course produced a most beneficial effect upon all branches of manufacture in which the acid is employed.

The large quantity of hydrochloric acid obtained as a secondary product has been employed for the preparation of bleaching powder, and the important arts of bleaching and calico-printing have thence received a considerable impulse. These arts have also derived a more direct benefit from the increased supply of sodium carbonate, which is so largely used for cleansing all kinds of textile fabrics. The manufactures of soap and glass, which probably create the greatest demand for sodium carbonate, have been increased and improved beyond all precedent by the production of this salt from native sources.

Sodium sulphate is converted into a mixture of carbonate and sulphide by being strongly heated with carbon only—

$$3\ Na_2SO_4 + C_6 = Na_2CO_3 + Na_2S_2 + Na_2S + 4CO_2 + CO.$$

Weldon melts Na_2SO_4 in a Siemens accumulating furnace, and pours it on to red-hot coal in a revolving furnace. The sodium sulphide so produced is converted into caustic soda by superheated steam; $Na_2S + 2H_2O = H_2S + 2NaHO$.

Hargreave's process dispenses with the use of sulphuric acid, and converts the sodium chloride into sulphate by the action of sulphurous acid gas (obtained by burning pyrites), steam, and air, at a dull red heat; $2NaCl + H_2O + SO_2 + O = Na_2SO_4 + 2HCl$. The hydrochloric acid is absorbed by water, as usual, and the sodium sulphate converted into carbonate as described above.

Deacon passes chlorine, sulphurous acid gas, and steam over the salt, which is made to glide down a series of inclined planes in a tower strongly heated; $SO_2 + 2H_2O + Cl_2 = 2HCl + H_2SO_4$. The HCl is condensed and employed for the production of chlorine, whilst the H_2SO_4 decomposes the NaCl.

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* Before evaporation, air is generally blown through the liquor to oxidise the sodium sulphide which may remain unaltered (see p. 263, *Sodium hydrate*).

Ammonia soda process, or *Solvay's process*.—This important process for converting NaCl into Na_2CO_3, which promises entirely to supersede the Leblanc process, depends upon the reaction between sodium chloride and hydro-ammonium carbonate: $NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3$. A saturated solution of common salt is mixed with about one-fifth of its volume of ammonia (sp. gr. 0.88), and carbonic acid gas is passed into it, when the sodium bicarbonate is precipitated. The portion of CO_2 which escapes absorption, and carries off NH_3 with it, is passed through a tall vertical cylinder with perforated shelves, through which solution of NaCl trickles; this absorbs the gases, and deposits more sodium bicarbonate, which collects on the shelves. The sodium bicarbonate is heated to convert it into carbonate; $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. The NH_4Cl in the solution is decomposed by heating with magnesia, to recover the ammonia, which is used again; $2NH_4Cl + MgO = 2NH_3 + H_2O + MgCl_2$. The solution of magnesium chloride is evaporated, and the residue strongly heated, when HCl is evolved and may be absorbed by water, and MgO is left, which may be used again.

A modification of this process consists in employing sodium sulphate (*salt-cake*) instead of sodium chloride; $Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O = 2NaHCO_3 + (NH_4)_2SO_4$. The ammonium sulphate is then fused with more salt-cake, and steam injected; $(NH_4)_2SO_4 + Na_2SO_4 = 2NH_3 + 2NaHSO_4$. The ammonia is used over again, and the $NaHSO_4$ is converted into salt-cake by fusion with common salt—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The sodium carbonate obtained by the ammonia process is much prized by the glass manufacturer on account of its purity.

Recovery of sulphur from alkali-waste.—Since nearly the whole of the sulphur which is employed, in the form of sulphuric acid, for decomposing the common salt, is obtained at the alkali-works in the form of calcium sulphide in the *tank-waste* left after exhausting the black ash with water, several processes have been devised for recovering the sulphur in order to employ it again for the manufacture of oil of vitriol. The simplest of these consists in blowing air through the moist tank-waste, until it is converted into a mixture of calcium disulphide and calcium thiosulphate, the oxidation being stopped when one-third of the disulphide has been converted into thiosulphate—

$$(1)\ 2CaS + O = CaO + CaS_2. \qquad (2)\ CaS_2 + O_3 = CaS_2O_3.$$

When the yellow liquor thus obtained is decomposed by the muriatic acid from the alkali-works, the sulphur is precipitated—

$$CaS_2O_3 + 2CaS_2 + 6HCl = S_6 + 3CaCl_2 + 3H_2O.$$

In another process, the drainings from the heaps of alkali-waste exposed to rain are saturated with sulphurous acid gas from burning pyrites, when calcium thiosulphate is formed, and, on adding muriatic acid, both the sulphur of the waste and that obtained from the pyrites are precipitated.

An objection to these processes appears to be the difficulty in procuring a sufficient quantity of muriatic acid, for which there is a great demand on the part of the producers of bleaching powder and bicarbonate of soda.

Another process for recovering the sulphur employs the waste liquor from the chlorine stills (see p. 148), which contains manganese dichloride ($MnCl_2$) and ferric chloride (Fe_2Cl_6). On treating the calcium sulphide in the soda-waste with this still-liquor, calcium chloride and sulphides of iron and manganese are produced; $MnCl_2 + CaS = MnS + CaCl_2$; $Fe_2Cl_6 + 3CaS = Fe_2S_3 + 3CaCl_2$.

By exposing these sulphides to the air, in a moist state, the sulphur is separated, and the metals are converted into oxides—

$$2MnS + O_3 = Mn_2O_3 + S_2; \quad Fe_2S_3 + O_3 = Fe_2O_3 + S_3.$$

By stirring these oxides with more soda-waste, the sulphides are reproduced, and are afterwards again oxidised by exposure to air so as to separate their sulphur. The sulphur thus separated combines with the calcium sulphide in a fresh portion of the waste, to form disulphide, one-third of which is oxidised by the air, as in the process first described, and converted into calcium thiosulphate. In order to precipitate the sulphur from the liquor containing the calcium disulphide and calcium thiosulphate, the excess of hydrochloric acid always present in the chlorine still-liquor is turned to account; the sulphur liquor is run into this until the precipitated sulphur begins to be accompanied by a black precipitate of sulphide of iron, showing that all the free acid has been neutralised. The still-liquor thus neutralised is then employed for decomposing a fresh portion of the soda-waste, as at the commencement of the process. The precipitated sulphur is pressed to free it from the liquor, dried, and melted by super-heated steam.

Although the chemistry of this process is rather elaborate, the practical working is said to be very simple and inexpensive.

A more direct process for extracting sulphur from tank-waste consists in decomposing the calcium sulphide in the waste with a strong solution of magnesium chloride; $CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S$. The H_2S is burnt, and the SO_2 formed is converted into H_2SO_4 in the vitriol chambers (p. 203).

In order to recover the magnesium chloride, the mixture of $CaCl_2$ and MgO is treated, under pressure, with carbonic acid gas obtained from a lime kiln; $CaCl_2 + MgO + CO_2 = CaCO_3 + MgCl_2$. The magnesium chloride may therefore be used over and over again.

According to one of the latest processes, the waste is used for precipitating dicalcic phosphate from the solution of native $Ca_3(PO_4)_2$ in HCl. The evolved H_2S is made to act upon more waste mixed with water, when the CaS passes into solution as $Ca(HS)_2$. The solution is evaporated, when $Ca(HS)_2 + 2H_2O = Ca(HO)_2 + 2H_2S$. The H_2S mixed with a carefully regulated amount of air is burnt in a kiln containing a deep bed of porous material, so that the H burns and the S separates in vapour, which is condensed.

Sodium carbonate, washing soda, $Na_2CO_3.10Aq$.—The crystals of sodium carbonate are easily distinguished by their property of efflorescing in dry air (p. 44), and by their alkaline taste, which is much milder than that of potassium carbonate, this being, moreover, a deliquescent salt. The crystals are very soluble in water, requiring only 2 parts of cold, and less than their own weight of boiling water; the solution is strongly alkaline to test-papers. The crystals fuse at 50° C., evolve steam, and deposit a granular powder of the composition $Na_2CO_3.Aq$. At a higher temperature it becomes Na_2CO_3, and fuses at a red heat.

If a solution of sodium carbonate be crystallised between 30° and 50° C., the crystals are $Na_2CO_3.7Aq$.

Bicarbonate of soda, or *hydro-sodium carbonate*, $NaHCO_3$, is the substance commonly used in medicine as carbonate of soda. It is prepared either by saturating the crystallised carbonate with CO_2, or by passing CO_2 through a strong solution of common salt mixed with ammonia (see p. 262).* It forms small prismatic crystals much less easily dissolved by water (8.85 per cent. at 15° C.) than the carbonate. The solution is much less alkaline. When the solution is heated it evolves CO_2, and crystals of the *sesquicarbonate*, $Na_2CO_3.2NaHCO_3.3Aq$, may be obtained from it. This salt is the *Trona* found in Africa and South America. It has been seen that, when strongly heated,

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Potassio-sodium carbonate, $KNaCO_3.6Aq$, may be crystallised from a mixture of solutions of the carbonates.

Soda lye, employed in the manufacture of hard soap, is a solution of *sodium hydrate* (NaHO), obtained by decomposing the carbonate with calcium hydrate (slaked lime); $Na_2CO_3 + Ca(HO)_2 = 2NaHO + CaCO_3$.

The solid sodium hydrate of commerce is generally obtained in the process for manufacturing carbonate of soda just described: the solution obtained by treating the black ash with water is concentrated by evaporation, so that the carbonate, sulphate, and chloride of sodium may crystallise out, leaving the hydrate, which is far more soluble, in the liquid. The latter, which still contains a compound of sulphide of sodium and sulphide of iron, which gives it a red colour (*red liquor*), is mixed with some nitrate of soda to oxidise the sulphides, and evaporated down until a fused mass of sodium hydrate is left, which is poured out into iron moulds.*

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* A saturated solution of NaCl mixed with one-third of its volume of NH_3 (sp. gr. .88) and saturated with CO_2 gives a copious precipitate of $NaHCO_3$.

Crystals of $2NaHO.7H_2O$ have been obtained.

Kryolite (Na_3AlF_6) is sometimes employed as a source of sodium hydrate, which may be obtained by decomposing it with slaked lime.

184. *Sodium.*—Potash and soda exhibit so much similarity in their properties that we cannot be surprised at their having been confounded together by the earlier chemists, and it was not till 1736 that Du Hamel pointed out the difference between them. The discovery of potassium naturally led Davy to that of sodium, which can be obtained by processes exactly similar to those adopted for procuring potassium, to which it will be remembered sodium presents very great similarity in properties (p. 15). Sodium, however, is readily distinguished from potassium by its burning with a yellow flame, which serves even to characterise it when in combination.

This yellow flame is well seen by dissolving salt in water in a plate, and adding enough spirit of wine to render it inflammable, the mixture being well stirred while burning. If a little piece of sodium be burnt in an iron spoon held in a flame, all the flames in the room, even at a remote distance, will be tinged yellow. The blowpipe-flame may also be employed to detect sodium by this colour, as in the case of potassium (p. 255). In fireworks, nitrate of soda is employed for producing yellow flames. A very good *yellow fire* may be made by intimately mixing, in a mortar, 74 grs. of nitrate of soda, 20 grs. of sulphur, 6 grs. of sulphide of antimony, and 2 grs. of charcoal, all carefully dried, and very finely powdered.

Sodium is a whiter metal than potassium. When heated in air, it gives a mixture of Na_2O and Na_2O_2, which are converted into $NaHO$ by water, O being evolved from the Na_2O_2. If water be gradually added to Na_2O_2, it dissolves, and the solution yields crystals of $Na_2O_2.8H_2O$.

It is remarkable that sodium is not attacked by perfectly dry chlorine or bromine, but if a trace of aqueous vapour be present, combination takes place with violence.

The preparation of sodium, by distilling a mixture of sodium carbonate and charcoal, is much easier than that of potassium, for which reason sodium is far less costly than that metal, and has received applications, on the large scale, during the last few years, for the extraction of the metals aluminium and magnesium. An amalgam of sodium (p. 130) is also employed with advantage in extracting gold and silver from their ores. To obtain sodium in large quantity, a mixture of dried carbonate of soda, powdered coal, and chalk is distilled in iron cylinders, when the sodium passes over in the form of vapour; $Na_2CO_3 + C_2 = Na_2 + 3CO$.

The chalk is employed to prevent the fusion of the mixture.

A greatly improved process for the manufacture of sodium (*Castner's process*) consists in distilling fused sodium hydrate in cast-iron crucibles, with a mixture of carbon and finely divided iron prepared by reducing hæmatite with CO or H, mixing it with tar, and coking, thus obtaining a mixture of 30 parts of carbon and 70 parts of iron. The reduction of the sodium is effected by the carbon, the iron serving to keep it down below the surface, and therefore in direct contact with the fused hydrate; $3NaHO + C_2 = Na_3 + CO + CO_2 + H_3$. The residues in the crucibles are treated with warm water, and the solution evaporated to recover some unreduced sodium carbonate, while the iron is dried, mixed with tar, and used over again. The distillation is carried on in a gas-furnace at a temperature of about 1000° C. It is said to yield 90 per cent. of the sodium present instead of 30 per cent. from the old process.

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* Another plan of treating the black ash liquor consists in allowing it to trickle through a column of coke against a current of air, when the sodium sulphide is oxidised, whilst the sulphide of iron is deposited. The liquor is mixed with a little chloride of lime to oxidise any remaining sulphides, and concentrated by evaporation, when carbonate and ferrocyanide of sodium are deposited in crystals. The liquor separated from these contains the sodium hydrate, and is evaporated till it solidifies on cooling.

The production of cheap sodium will lower the price of aluminium and magnesium, which are extracted by its aid.

Sodium chloride, $NaCl$, forms rock salt and *table salt*, the latter consisting of minute crystals formed by boiling down the water of brine springs (see p. 258). It forms cubical crystals, almost equally soluble in hot and cold water; 100 parts of water at 15° C. dissolve 36 parts of salt, at 100°, 39 parts. It is insoluble in alcohol. At a red heat it fuses, and is afterwards vaporised. It forms two *cryohydrates*, $NaCl.2Aq$, deposited from a saturated solution cooled to $-10°$ C., and $NaCl.10Aq$, deposited at $-22°$. They are decomposed at higher temperatures.

Sodium fluoride, NaF, in which half the sodium is replaced by aluminium, is found as *cryolite*, $AlNa_3F_6$.

The *sulphides of sodium* are similar to those of potassium. *Sodium sulphate* is found anhydrous as *Thénardite*. Crystallised sodium sulphate, $Na_2SO_4.10Aq$, or *Glauber's salt*, is made by decomposing $2NaCl$ with H_2SO_4, dissolving and crystallising. It forms prismatic crystals which effloresce in air, fuse at 33° C., and become anhydrous at 100°. It is more soluble in water at 33° C. than at any other temperature, 100 parts of water dissolving 115 parts of the crystals. When this solution is heated, it deposits octahedral crystals of $Na_2SO_4.Aq$. When cooled quietly in a covered vessel, the solution exhibits, in a high degree, the phenomenon of *supersaturation*, so that a crystal of the salt must be dropped in to cause crystallisation, or the immersion of a dusty glass rod will often answer, the dust probably containing minute crystalline particles. At 12° C. crystals of $Na_2SO_4.7Aq$ may be obtained. The crystals of $Na_2SO_4.10Aq$, with half their weight of strong HCl, form an excellent freezing mixture, being equivalent to salt and ice—

$$Na_2SO_4.10Aq + HCl = NaHSO_4 + NaCl + 10Aq.$$

Crystallised sodium sulphate forms the very common saline efflorescence upon the surface of brick walls, and has been found covering the sandy soil of the Desert of Atacama over a considerable area.

Glauberite is $Na_2Ca(SO_4)_2$, and is nearly insoluble in water.

Hydrosodium sulphate, $NaHSO_4$, or *bisulphate of soda*, crystallises in prisms with 1Aq. It is more fusible and more easily decomposed by heat than $KHSO_4$. It is decomposed by alcohol into H_2SO_4 and Na_2SO_4, which remains undissolved.

When moderately heated, $2NaHSO_4 = H_2O + Na_2S_2O_7$ (*pyrosulphate*), decomposed by a red heat into Na_2SO_4 and SO_3. Sodium pyrosulphate is also formed when $NaCl$ is heated with SO_3—

$$2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2.$$

Sodium sulphite crystallises in prisms, $Na_2SO_3.7Aq$, which are very soluble in water, yielding an alkaline solution. It is prepared by saturating one-half of a solution of Na_2CO_3 with SO_2 gas, and adding the other half—

$$(1)\ Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2;$$
$$(2)\ 2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2.$$

The sodium sulphite is useful in the laboratory as a reducing agent, and the hydrosodium sulphite, $NaHSO_3$, is used in organic chemistry.

Sodium thiosulphate, $Na_2S_2O_3$, or *hyposulphite of soda*, crystallises in glassy prisms, $Na_2S_2O_3.5Aq$, which are very fusible, and remain liquid after cooling until a minute crystal of the salt is dropped in, when the whole crystallises in a most beautiful way. The salt is very soluble in water, but insoluble in alcohol. When the crystals are heated in the air, they dry up, and the residue burns with a blue flame; $Na_2S_2O_3 + O_3 = Na_2SO_4 + SO_2$. But if the salt be heated in a tube or flask so that air is excluded, it leaves an orange-coloured residue of sodium pentasulphide mixed with sodium sulphate; $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$. On a small scale, sodium thiosulphate may be obtained by dissolving sulphur in a boiling solution of sodium sulphite, and crystallising. On the large scale, it is made from the calcium sulphide contained in the *tank-waste* from the alkali-works, which is oxidised by air and decomposed by sodium sulphate—

$$(1)\ 2CaS + 2O_2 + H_2O = CaS_2O_3 + Ca(HO)_2;$$
$$(2)\ CaS_2O_3 + Na_2SO_4 = CaSO_4 + Na_2S_2O_3.$$

The calcium sulphate, being sparingly soluble, is easily separated.

Sodium thiosulphate is much used in photography for fixing prints by dissolving the unaltered portion of the sensitive film of silver chloride or iodide. It is also used by bleachers as an *antichlore* (see p. 200).

Phosphate of soda, or *hydro-disodium phosphate*, HNa_2PO_4, crystallises in prisms, $Na_2HPO_4.12Aq$, which effloresce in air and dissolve easily in water, giving an alkaline solution. When heated, they fuse easily, and lose the 12Aq at 45° C.; at a red heat, $2Na_2HPO_4 = H_2O + Na_4P_2O_7$ (*pyrophosphate*).

Na_2HPO_4 occurs in the blood and in urine. It is prepared by decomposing bone-ash, which contains $Ca_3(PO_4)_2$, with H_2SO_4, so as to obtain the insoluble $CaSO_4$ and a solution of impure H_3PO_4. This is decomposed by Na_2CO_3, the solution filtered from the small quantity of $CaCO_3$, evaporated and crystallised—

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2.$$

Arseniate of soda, or *hydro-disodium arsenate*, HNa_2AsO_4, forms crystals with 12Aq, resembling those of the phosphate, but the salt as commonly sold contains 7Aq. There exists also the salt $Na_2HPO_4.7Aq$, but this is not that commonly sold.

Sodium arsenate is made by dissolving white arsenic in caustic soda, adding sodium nitrate, evaporating to dryness, heating the residue to redness and dissolving in water—

$$(1)\ As_2O_3 + 6NaHO = 2Na_3AsO_3 + 3H_2O;$$
$$(2)\ Na_3AsO_3 + NaNO_3 = Na_3AsO_4 + NaNO_2;$$
$$(3)\ Na_3AsO_4 + H_2O = Na_2HAsO_4 + NaHO.$$

185. *Borax*, *biborate of soda* ($Na_2O.2B_2O_3$), or *sodium pyroborate* ($Na_2B_4O_7$).—It has already been stated that borax is deposited during the evaporation of the waters of certain lakes in Thibet, whence it is imported into this country in impure crystals, which are covered with a peculiar greasy coating. Borax has also been found abundantly in Southern California. The refiner of tincal powders the crystals and washes them, upon a strainer, with a weak solution of soda, which converts the greasy matter into a soap and dissolves it. The borax is then dissolved in water, a quantity of sodium carbonate is added to separate some lime which the borax usually contains, and, after filtering off the carbonate of lime, the solution is evaporated to the crystallising

point and allowed to cool, in order that it may deposit the pure crystals of borax.

It appears, however, that the greater part of the borax employed in the arts is manufactured in this country by heating sodium carbonate with boric acid, when the latter expels the carbonic acid.* The mass is then dissolved in water, and the borax crystallised, an operation upon which much care is bestowed, since the product does not meet with a ready sale unless in large crystals.

The solution of borax, having been evaporated to the requisite degree of concentration, is allowed to crystallise in covered wooden boxes, which are lined with lead and enclosed in an outer case of wood, the space between the sides of the case and the box being stuffed with some bad conductor of heat, so that the solution of borax may cool very slowly, and large crystals may be deposited. In about thirty hours the crystallisation is completed, when the liquid is drawn off as rapidly as possible, the last portion being carefully soaked up with sponges, so that no small crystals may be afterwards formed upon the surface of the large ones; the case is then again covered up, so that the crystals may cool slowly without cracking. When a solution of borax is crystallised above 60° C., it yields *octahedral borax*, $Na_2B_4O_7.5Aq$, which is also deposited when solution of prismatic borax is evaporated *in vacuo*.

Borax is chemically known as *sodium pyroborate* (p. 120), and is represented, in the dry state, by the formula $Na_2B_4O_7$. The ordinary prismatic crystals, however, contain ten molecules of water of crystallisation, and are therefore represented by the formula $Na_2B_4O_7.10Aq$. They soon effloresce and become opaque when exposed to air, and may readily be distinguished by their alkaline taste and action upon test-papers, and especially by their behaviour when heated, for they fuse easily and *intumesce* most violently, swelling up to a white spongy mass of many times their original bulk; this mass afterwards fuses down to a clear liquid which forms a transparent glassy mass on cooling (*vitrefied borax*), and since this glass is capable of dissolving many metallic oxides with great readiness (borax being, by constitution, an acid salt, and therefore ready to combine with more base), it is much used in the metallurgic arts. Large quantities of borax are also employed in glazing stoneware.

A dilute solution of borax dissolves iodine to a colourless solution, but, on concentration, the iodine is precipitated; probably the borax is decomposed in the dilute solution into boric acid and soda, which converts the iodine into iodide and iodate; on concentrating, the boric acid liberates hydriodic and iodic acids, which react with each other, separating iodine.

Sodium silicate.—A combination of soda with silica has long been used, under the name of *soluble glass*, for imparting a fire-proof character to wood and other materials, and, more recently, for producing artificial stone for building purposes, and for a peculiar kind of permanent fresco-painting (*stereochromy*), the results of which are intended to withstand exposure to the weather.

Soluble glass is usually prepared by fusing 15 parts of sand with

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* The ammonia which is evolved from the Tuscan boracic acid employed in this process is known in commerce as *Volcanic ammonia*, and is free from the empyreumatic odour which generally accompanies that from coal and bones.

8 parts of carbonate of soda and 1 part of charcoal. The silicic acid, combining with the soda, disengages the carbonic acid gas, the expulsion of which is facilitated by the presence of charcoal, which converts it into carbonic oxide. The mass thus formed is scarcely affected by cold water, but dissolves when boiled with water, yielding a strongly alkaline liquid.

In using this substance for rendering wood fire-proof, a rather weak solution is first applied to the wood, and over this a coating of lime-wash is laid; a second coating of soluble glass (in a more concentrated solution) is then applied. The wood so prepared is, of course, charred, as usual, by the application of heat, but its inflammability is remarkably diminished.

For the manufacture of *Ransome's artificial stone*, the soluble glass is prepared by heating flints, under pressure, with a strong solution of caustic soda, to a temperature between 300° and 400° F., when the silica constituting the flint enters into combination with the soda. Finely divided sand is moistened with this solution, pressed into moulds, dried, and exposed to a high temperature, when the silicate of soda fuses and cements the grains of sand together into a mass of artificial sandstone, to which any required colour may be imparted by mixing metallic oxides with the sand before it is moulded.

Silicate of soda is also sometimes used as a *dung substitute* (p. 241) in calico-printing.

Di-sodium silicate has been obtained in prismatic crystals, $Na_2SiO_3.8Aq$, by dissolving silica in caustic soda. It is soluble in water, and the solution is decomposed by the CO_2 in the air. When amorphous silica is dissolved in a hot solution of Na_2CO_3, the liquid becomes a jelly on cooling.

Sodium nitrate, $NaNO_3$, will be more particularly noticed in the section on gunpowder. It is imported from Peru, and used in considerable quantity as a manure, and for the manufacture of potassium nitrate.

SALTS OF AMMONIUM.

186. The great chemical resemblance between some of the salts formed by neutralising acids with ammonia, and the salts of potassium and sodium, has been already pointed out as affording a reason for the hypothesis of the existence of a compound metal, *ammonium* (NH_4), equivalent in its functions to potassium and sodium.

The compounds which are formed when ammonia (NH_3) combines with the anhydrides, such as carbonic (CO_2) and sulphuric (SO_3), do not exhibit the resemblance to the salts of potassium and sodium until water is added. Thus, by the action of dry ammonia gas upon sulphuric anhydride, a compound called *sulphuric ammonide* is formed, having the composition $(NH_3)_2SO_3$. This substance dissolves in water and crystallises in octahedra, but its solution is not precipitated by barium chloride, which always precipitates the true sulphates, nor by platinic chloride, which precipitates the true ammonium salts. By long boiling with water, however, it becomes converted into ammonium sulphate, $(NH_4)_2SO_4$, which yields precipitates with both the above tests.* The phosphoric, carbonic, and sulphurous anhydrides also combine with dry ammonia to form ammonides, which do not respond to the ordinary tests for the corresponding salts of ammonium until after water has been assimilated. The true salts of ammonium are produced either by the combination of an acid with ammonia, or by double decomposition.

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* Representing sulphuric acid as sulphuryl hydrate, $SO_2.OH.OH$, ammonium sulphate is $SO_2.ONH_4.ONH_4$, and sulphuric ammonide is $SO_2.NH_2.ONH_4$, the amidogen group, NH_2, replacing the ammon-oxyl group, $O(NH_4)$.

Ammonium hydrate, NH_4HO, is believed to exist in the solution of ammonia; $NH_3 + H_2O = NH_4HO$; but it has not been obtained in the separate state.

Ammonium nitrate, NH_4NO_3, is prepared by neutralising ordinary nitric acid with lumps of ammonium carbonate, when the nitrate crystallises on cooling in six-sided prisms like those of KNO_3, but they are deliquescent and very soluble in water. When gently heated, it melts at 150° C., and is decomposed at 210° C., when it boils and passes off entirely as water and nitrous oxide; $NH_4NO_3 = 2H_2O + N_2O$. If sharply heated, as by throwing it on a red-hot surface, it deflagrates. If very carefully heated, it may be sublimed. It is largely used for making nitrous oxide.

Ammonium nitrate absorbs one-third of its weight of ammonia and becomes liquid; the ammonia is expelled at 25° C.

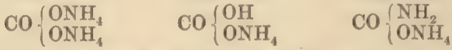
Ammonium nitrite, NH_4NO_2, is interesting on account of its easy decomposition by heat; $NH_4NO_2 = N_2 + 2H_2O$. This takes place even on boiling the solution, so that a mixture of solutions of potassium nitrite and ammonium chloride is used for preparing nitrogen. Ammonium nitrite is found, in very small quantity, in rain water; it can also be detected in the water condensed from hydrogen burning in air. Ammonia is partly converted into this salt when oxidised by ozone or even by air in presence of heated platinum; $2NH_3 + O_3 = NH_4NO_2 + H_2O$.

187. *Ammonium sulphate*, $(NH_4)_2SO_4$, is largely employed in the preparation of ammonia-alum, and of artificial manures, for which purposes it is generally obtained from the ammoniacal liquor of the gas-works by neutralising with sulphuric acid and evaporating. The rough crystals are gently heated to expel tarry substances, and purified by recrystallisation. The crystals have the same shape as those of potassium sulphate, and are easily soluble in water, but not in alcohol. When heated to about 500° F. (260° C.), the ammonium sulphate is decomposed, yielding vapour of ammonium sulphite, water, ammonia, nitrogen, and sulphur dioxide. If muslin be dipped into a solution of ammonium sulphate in ten parts of water and dried, it will no longer burn with flame when ignited. The mineral *mascagnine* consists of ammonium sulphate. This salt is occasionally found in needle-like crystals upon the windows of rooms in which coal gas is burnt.

188. *Ammonium carbonate*, also called *smelling salts* or *Preston salts*, is largely used in medicine, and by bakers and confectioners, for imparting lightness or porosity to cakes, &c. It is commonly prepared by mixing sal ammoniac (ammonium chloride) with twice its weight of chalk, and distilling the mixture in an earthen or iron retort, communicating, through an iron pipe, with a leaden chamber or receiver, in which the ammonium carbonate collects as a transparent fibrous mass, which is extracted by taking the receiver to pieces, and purified by resubliming it in iron vessels surmounted by leaden domes. The action of calcium carbonate upon ammonium chloride would be expected to furnish the normal carbonate, $(NH_4)_2CO_3$, but this salt (even if produced)

is decomposed by the heat employed in the process into *hydro-ammonium carbonate* and *ammonium carbamate* ; (1) $(NH_4)_2CO_3 = HNH_4CO_3 + NH_3$; (2) $(NH_4)_2CO_3 = NH_4CO_2NH_2 + H_2O$.

Normal ammonium carbonate. Hydro-ammonium carbonate. Ammonium carbamate.



$$CO\left\{\begin{matrix}ONH_4\\ONH_4\end{matrix}\right. \qquad CO\left\{\begin{matrix}OH\\ONH_4\end{matrix}\right. \qquad CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$$

The commercial carbonate is usually a mixture of $2NH_4HCO_3$ and $NH_4CO_2NH_2$. By treating it with strong alcohol, the carbamate is dissolved and the hydro-ammonium carbonate is left.

When exposed to the air, it smells of ammonia, and gradually becomes NH_4HCO_3, the carbamate being decomposed and volatilised; $NH_4CO_2NH_2 = CO_2 + 2NH_3$. On treating the commercial carbonate with a little water, the hydro-ammonium carbonate is left undissolved, whilst the carbamate is converted into carbonate and dissolved; $NH_4CO_2NH_2 + H_2O = (NH_4)_2CO_3$.

Ammonium carbonate, $(NH_4)_2CO_3$, is obtained in crystals by treating the commercial carbonate with strong ammonia. The crystals contain 1Aq. They are deliquescent in air, and evolve NH_3, becoming converted into the bicarbonate; $(NH_4)_2CO_3 = NH_3 + NH_4HCO_3$.

Ammonium bicarbonate, NH_4HCO_3, or hydro-ammonium carbonate, is the most stable, and is obtained by dissolving the commercial carbonate in a little boiling water, when it crystallises out on cooling. It has been found in considerable quantity, forming crystalline masses, in a bed of guano on the western coast of Patagonia.

Sal volatile is an alcoholic solution of ammonium carbonate and carbamate.

The *ammonium carbamate* is deposited as a white solid when ammonia gas is mixed with carbonic acid gas. It may be obtained in crystals by passing CO_2 and NH_3 into the strongest solution of ammonia.

Ammonium carbamate is easily soluble in water, which soon converts it into ammonium carbonate. The aqueous solution, when freshly prepared, is not precipitated by calcium chloride, but the calcium carbonate is deposited on standing or heating.

When ammonium carbamate is heated in a sealed tube to 130° C. it is decomposed into ammonium carbonate and urea; $2NH_4CO_2NH_2 = (NH_4)_2CO_3 + CON_2H_4$. Carbamic acid, HCO_2NH_2, has not been isolated; its relation to carbonic acid is seen by a comparison of their formulæ; carbonic acid, CO.OH.OH; carbamic acid, $CO.OH.NH_2$. Other carbamates have been obtained by passing CO_2 through strongly ammoniacal solutions of different bases, and precipitating the carbamates by alcohol. When potassium carbamate is heated, it yields water and potassium cyanate; $KCO_2NH_2 = KCNO + H_2O$.

Carbamates are remarkable for evolving nitrogen when treated with a mixture of soda and sodium hypobromite, but *not with the hypochlorite;* thus sodium carbamate, with sodium hypobromite and soda, gives sodium carbonate, sodium bromide, water, and nitrogen—

$$2(CO.NH_2.ONa) + 3NaBrO + 2NaOH = 2CO(ONa)_2 + 3NaBr + 3H_2O + N_2.$$

If solution of sodium carbamate be mixed with sodium hypochlorite and soda, no nitrogen is evolved until a soluble bromide is added, a reaction which will indicate bromides even in dilute solutions. The solution of sodium carbamate may be prepared by dissolving ammonium carbamate in a strong solution of soda, and allowing the mixture to stand over strong sulphuric acid under a bell-jar for a day or two.

189. *Ammonium chloride* (NH_4Cl), also called *muriate of ammonia* and *sal ammoniac.*—When dry ammonia gas is brought in contact with an equal volume of dry hydrochloric acid gas, it has been seen (p. 129) that they combine directly to produce this salt, the preparation of which on the large scale has been noticed at p. 124. It is also some-

times made by subliming a mixture of ammonium sulphate with common salt; $(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4$; or by boiling the *ammoniacal liquor* from the gas-works with lime and passing the NH_3 into HCl, when impure crystals of NH_4Cl are obtained, which are purified by sublimation from an iron pan into an iron dome. Its commercial form is that of a very tough translucent fibrous mass, generally of the dome-like shape of the receivers, and often striped with brown, from the presence of a little iron. It has not the least smell of ammonia, and is very soluble in water, requiring about three parts of cold water, and little more than its own weight of boiling water. As the hot solution cools, it deposits beautiful fern-like crystallisations composed of minute cubes and octahedra. The liquefaction of sal ammoniac in water lowers the temperature very considerably, which renders the salt very useful in freezing mixtures. A mixture of equal weights of sal ammoniac and nitre, dissolved in its own weight of water, lowers the temperature of the latter from 50° F. to 10°. In this case partial decomposition takes place, resulting in the production of potassium chloride and ammonium nitrate, both of which absorb much heat whilst being dissolved by water. The solution of ammonium chloride in water is slightly acid to blue litmus-paper. When sal ammoniac is heated, it passes off in vapour, at a temperature below redness, without previously fusing; the vapour forms thick white clouds in the air, and may be recondensed as a white crust upon a cold surface; but it cannot be sublimed without some loss, a portion being decomposed into hydrochloric acid, hydrogen, and nitrogen.

The specific gravity (weight of 1 volume) of the vapour of sal ammoniac is 13.3 times that of hydrogen, so that 53.5 parts, or one molecule, would appear to occupy 4 volumes instead of 2, but this may be explained by supposing a temporary *dissociation* of the hydrochloric acid and ammonia when the salt is converted into vapour, so that the observed specific gravity is really that of a mixture of equal volumes of these constituent gases. Experimental evidence has been obtained in support of this view, for it has been found that free ammonia and hydrochloric acid may be separated by diffusion from the vapour obtained on heating ammonium chloride.

This may be shown by placing a fragment of sal ammoniac in a narrow test-tube, with a plug of asbestos at a little distance above it; if a piece of red litmus-paper be placed in the tube, it will be found, on heating the sal ammoniac and the asbestos, that the NH_3, being lighter, diffuses most rapidly through the asbestos, and blues the red litmus, but soon afterwards the hydrochloric acid diffuses through, and the litmus is again reddened.

Moreover, the heat which becomes latent or is *absorbed* in vaporising the sal ammoniac, is almost exactly that which is *produced* by the combination of the hydrochloric acid and ammonia.

When ammonium chloride is heated with metallic oxides, the hydrochloric acid often converts the oxide into a chloride which is either fusible or volatile, so that sal ammoniac is often employed for cleansing the surfaces of metals previously to soldering them. Even those metallic oxides which are destitute of basic properties, such as antimonic and stannic oxides, are convertible into chlorides by the action of sal ammoniac at a high temperature.

Ammonium chloride is found in volcanic districts, and is present in very small quantity in sea water.

190. *Hydrosulphate of ammonia*, $(2NH_3)H_2S$, or *ammonium sulphide*

$(NH_4)_2S$, has been obtained in colourless crystals by mixing hydrosulphuric acid gas with twice its volume of ammonia gas in a vessel cooled by a mixture of ice and salt. It is a very unstable compound, decomposing at the ordinary temperature of the air into free ammonia and *ammonium hydrosulphide*, NH_4HS, which may be obtained in very volatile colourless needles by passing equal volumes of NH_3 and H_2S into a vessel cooled in ice, or by passing H_2S gas into an alcoholic solution of ammonia, when it crystallises in colourless plates which undergo dissociation into NH_3 and H_2S when vaporised. When a solution of ammonia is saturated with hydric sulphide, a colourless solution of the *ammonium hydrosulphide* (NH_4HS) is formed. The solution soon becomes yellow in contact with the air, from the formation of *ammonium disulphide*, $(NH_4)_2S_2$, ammonium thiosulphate being formed at the same time; $4NH_4HS + O_5 = (NH_4)_2S_2 + (NH_4)_2S_2O_3 + 2H_2O$. Eventually, the solution deposits sulphur and becomes colourless, thiosulphate, sulphite, and sulphate of ammonium being formed. When the freshly prepared colourless solution of ammonium hydrosulphide is mixed with an acid, the solution remains clear, hydrosulphuric acid being evolved with effervescence; $NH_4HS + HCl = NH_4Cl + H_2S$; but if the solution be yellow, a milky precipitate of sulphur is produced, from the decomposition of the ammonium disulphide; $(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S$.

The fresh solution gives a black precipitate of lead sulphide when solution of lead acetate is added to it, but after it has been kept till it is of a dark yellow or red colour, it gives a red precipitate of the persulphide of lead. Solution of ammonium sulphide, prepared by mixing the hydrosulphide with an equal volume of solution of ammonia, is largely employed in analytical chemistry; $NH_4HS + NH_3 = (NH_4)_2S$. The solution has a very disagreeable odour.

Ammonium disulphide is obtained in deliquescent yellow crystals, when a mixture of ammonia gas with vapour of sulphur is passed through a red-hot porcelain tube. It is the chief constituent of *Boyle's fuming liquor*, a fetid yellow liquid obtained by distilling sal ammoniac with sulphur and lime. The disulphide is sometimes deposited in yellow crystals from this liquid. By dissolving sulphur in ammonium disulphide, orange-yellow prismatic crystals of *ammonium pentasulphide*, $(NH_4)_2S_5$, may be obtained. $(NH_4)_2S_4$ and $(NH_4)_2S_7$ have been crystallised.

It is scarcely possible to represent the constitution of the higher sulphides of ammonium except on the ammonium hypothesis.

Ammonium bromide (NH_4Br) and *ammonium iodide* (NH_4I) are useful in photography. They are both colourless crystalline salts, but the iodide is very liable to become yellow or brown, from the separation of iodine, unless kept dry and in the dark. Both salts are extremely soluble in water.

Microcosmic salt, or *phosphorus salt*, or *hydro-sodio-ammonium phosphate*, $HNaNH_4PO_4.4Aq$, is found in putrid urine and in guano. It is prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate—

$$Na_2HPO_4 + NH_4Cl = HNaNH_4PO_4 + NaCl.$$

It forms prismatic crystals which are very soluble and fusible, boiling violently when further heated, and finally leaving a transparent glass of sodium metaphosphate, which is valuable in blowpipe work for dissolving metallic oxides; $NaNH_4HPO_4 = NH_3 + H_2O + NaPO_3$.

191. LITHIUM ($Li = 7$ parts by weight) is a comparatively rare metal, obtained chiefly from the minerals *lepidolite* (λεπίς, *a scale*) or *lithia-mica*, containing silicate of alumina with fluorides of potassium and lithium; *petalite* (πέταλον, *a leaf*), silicate of soda, lithia, and alumina; and *triphane* or *spodumene* (σποδὸς, *ashes*), which has a similar composition. Its name (from λίθος, *a stone*) was bestowed in the belief that it existed only in the mineral kingdom, but recent investigation has detected it in minute proportion in the ashes of tobacco and other plants.

The water of a hot spring in Clifford United Mines, in Cornwall, contains 26 grains of lithium chloride per gallon.

Metallic lithium is obtained by decomposing fused lithium chloride by a galvanic current. It is remarkable as the lightest of the solid elements (sp. gr. 0.59). It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidised than those metals. It decomposes water rapidly at the ordinary temperature, but does not inflame upon it.

Lithium differs from potassium and sodium by forming a sparingly soluble phosphate (Li_3PO_4) and carbonate (Li_2CO_3). The compounds of lithium impart a red colour to the flame of the blowpipe (p. 257).

Lithium carbonate is occasionally employed medicinally.

RUBIDIUM ($Rb' = 85$ parts by weight) and CÆSIUM ($Cs' = 133$ parts by weight) were discovered in 1860, by Bunsen and Kirchhoff, during the analysis of a certain spring water which contained these metals in so minute quantity (2 or 3 grs. in a ton) that they would certainly have escaped observation if the analysis had been conducted in the ordinary way. The discovery of these metals, as well as of three others (thallium, indium, gallium) to be mentioned hereafter, was the result of the application of the method of *spectrum analysis*, of which a brief description is here given, although the discussion of the optical principles upon which it depends would be misplaced in a chemical work.

192. *Spectrum analysis.*—It has been mentioned above that compounds of potassium, sodium, and lithium impart, respectively, lilac, yellow, and red colours to the blowpipe flame (or air-gas flame, see p. 107), or, in other words, that the highly heated vapours of the metals evolve luminous rays of these particular colours. When the quantity of the metal is extremely minute, and its peculiar luminous rays proportionally scanty, their colour may very easily escape notice, especially if two or three metals are present in the flame at the same time. But if the light emanating from the flame be allowed to pass through a narrow slit at A (fig. 226), collected by a lens, and transmitted through a prism of flint glass or through a hollow prism (B) filled with carbon disulphide, all the rays of one colour will be refracted in a definite direction, so that an observer through the telescope at C will perceive as many images of the slit as there are colours in the flame. The ordinary flame of a gas burner, emitting a white light, will give a *continuous spectrum* composed of overlapping images of the slit in all the colours which make up white light; but if a Bunsen flame be employed, a single image will be seen, forming a bright yellow line in the place where the brightest yellow was seen in the continuous spectrum; this line is due to the presence of a little sodium in the flame, from the dust in the air, and it becomes very intense if a little sodium chloride be held in the flame on a loop of platinum wire. Heated sodium vapour emits yellow light only, but most other metallic vapours emit light composed of more than one colour, so that they give two or more coloured images of the slit in different parts of the spectrum (*bright line spectrum*). The heated vapour of lithium emits a mixture of red with a few yellow rays, and accordingly, the spectrum of a flame containing lithium exhibits a very bright band of red light, and a comparatively dull band of yellow light,

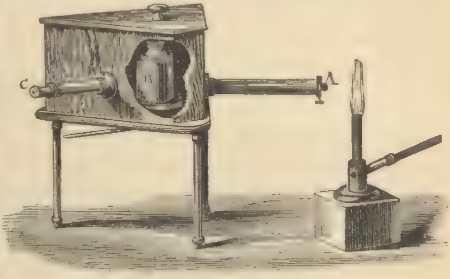
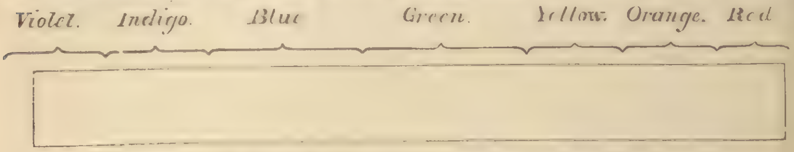
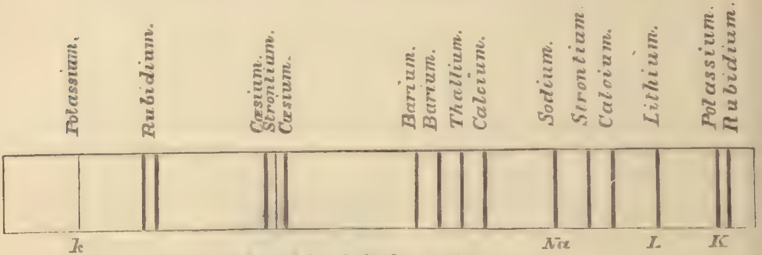


Fig. 226.—Spectroscope.

the red band being characteristic of lithium. The potassium flame emits a mixture of blue and red rays, so that its spectrum exhibits a distinct red band of a darker colour than the lithium band, and a feeble violet band. The *spectroscope* has now taken its place among the apparatus indispensable to the analytical chemist. The prism B may be slowly moved round by a handle attached to a stage on which it rests, in order that the different parts of the spectrum may be successively brought into sight. By comparing the spectra of the flames containing vapours of the metals with a picture or map of the solar spectrum (fig. 227), the exact position of the various coloured bands may be noted, and thus, if several metals are present in the same flame, they may still be distinguished by the colours and positions of their bands. Thus, if a mixture of the chlorides of potassium, sodium, and lithium be taken upon a loop of platinum wire and held in the flame, the dull red line of potassium (K, fig. 227) is seen close to one end of the spectrum; at some distance from it the bright red band (L) of lithium; at about the same distance from this, the pale yellow lithium line; and close to this, the bright yellow band of sodium (Na); whilst near the other end of the spectrum is the feeble violet band of potassium (*k*). The chlorides of the metals are most suitable for this experiment on account of their easy conversion into vapour.



Spectrum furnished by solar light decomposed by a prism.



Coloured bands in the spectrum.
Fig. 227.

Spark spectrum.—Several metals which do not yield a characteristic spectrum in the air-gas flame will do so at the much higher temperature of the electric spark, which decomposes the compounds of the metals, converts the metal into vapour, and renders the vapour incandescent. By introducing the material under examination into the apparently continuous spark between the terminals of an induction-coil (p. 12), and viewing the spark through the narrow opening of the spectroscope, the position of the bright lines may be measured, and the metal identified. It is often sufficient to employ platinum or aluminium wires as the terminals of the coil, and to moisten them with the solution of the metallic chloride to be tested.

Radiant matter spectroscopy.—The substance under examination is placed in a glass bulb, in the walls of which are sealed two platinum wires to serve as electrodes; these are situated near to the opposite openings of the bulb into the tube on which it is blown. One of the outer openings of this tube is hermetically sealed, and the other is drawn out to a capillary neck, by which it may be connected with a Sprengel air-pump, and exhausted till the vacuum is nearly perfect, when it is also hermetically sealed. On connecting the platinum wires with the terminals of an induction-coil, the bulb becomes illuminated by the discharge, and the substance, if a proper subject for the experiment, glows with a phosphorescent light, and, viewed through a spectroscope, exhibits some bright bands in the spectrum, from the colour and position of which the substance may be identified. By this method, Crookes detected *yttrium* in very minute quantity in a large number of minerals by the citron-coloured band visible between the green and yellow in the phosphorescence-spectrum of their sulphates; another very rare metal, *samarium*, was indicated by an orange band, seen under similar conditions.

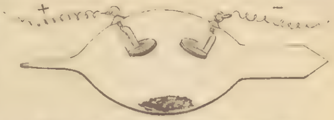


Fig. 228.—Radiant matter bulb.

When examining, with the spectroscope, the alkaline chlorides extracted from the spring water above alluded to, Bunsen and Kirchhoff observed two red and two blue bands in the spectrum, which they could not ascribe to any known substance, and which they ultimately traced to the two new metals, rubidium (*rubidus*, dark-red) and cæsium (*cæsius*, sky-blue).

Rubidium has since been found in small quantity in other mineral waters, in lepidolite, and in the ashes of many plants. This metal is closely related in properties to potassium, but is more easily fusible and convertible into vapour, and actually surpasses that metal in its attraction for oxygen, rubidium taking fire spontaneously in air. It burns on water with exactly the same flame as potassium. Its hydrate is a powerful alkali, like potash, and its salts are isomorphous with those of potassium. The double chloride of platinum and potassium, however, is eight times as soluble in boiling water as the corresponding salt of rubidium, which is taken advantage of in separating these two allied metals.

Cæsium appears to be even more highly electro-positive than rubidium, forming a strong alkali, cæsium hydrate, and salts which are isomorphous with those of potassium. Cæsium carbonate, however, is soluble in alcohol, which does not dissolve the carbonates of potassium and rubidium. Moreover, the cæsium bitartrate is nine times as soluble in water as the rubidium bitartrate.

Cæsium has been found in lepidolite; and the rare mineral *pollux* found in Elba, and resembling felspar in composition, is said to contain a very large quantity of this metal. The alum of the island of Vulcano is mentioned as a rich source of cæsium and rubidium.

Metallic cæsium cannot be obtained by reduction with carbon, but it has been extracted by decomposing its cyanide by the galvanic current.

193. *General review of the group of alkali metals.*—Cæsium, rubidium, potassium, sodium, and lithium constitute a group of elements conspicuous for their highly electro-positive character, the powerfully alkaline nature of their hydrates, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electro-negative group containing fluorine, chlorine, bromine, and iodine, and, like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electro-positive member, rubidium the next, then potassium and sodium, whilst lithium is the least electro-positive; and just as iodine, the least electro-negative of the halogens, possesses the highest atomic number, so cæsium, the least electro-negative (or most electro-positive) of the alkali-metals, has a higher

atomic weight than any other member of this group, their atomic weights being represented by the numbers, cæsium, 133; rubidium, 85.3; potassium, 39; sodium, 23; lithium, 7. As in the case of the halogens also, these are all univalent elements. Just as chlorine is accepted as the representative of *chlorous radicals*, so potassium is commonly regarded as the type of *basylous radicals*, the term radical being applied to all substances, whether elementary or compound, which are capable of being transferred, like chlorine or potassium, from one compound to another without suffering decomposition.

Some of the physical properties of these elements exhibit a gradation in the same order as their atomic weights; thus cæsium fuses at 27° C., rubidium at 38°, potassium at 63°, sodium at 97°, and lithium at 180°; at ordinary temperatures, rubidium is the softest, and lithium the hardest of these metals.

In some of their salts a similar gradational relation is observed; the carbonates, for example, of cæsium, rubidium, and potassium are highly deliquescent, absorbing water greedily from the air, while carbonate of sodium is not deliquescent, and carbonate of lithium is sparingly soluble in water. The difficult solubility of the carbonate and phosphate of lithium constitutes the connecting link between this and the succeeding group of metals, the carbonates and phosphates of which are insoluble in water.

BARIUM.

$Ba'' = 137$ parts by weight.

194. Barium, so named from the great weight of its compounds (*βαρύς*, *heavy*), is found in considerable abundance in the north of England, in two minerals known as *Witherite* (barium carbonate, $BaCO_3$) and *heavy spar* (barium sulphate, $BaSO_4$). Witherite is found in large masses in the lead-mines at Alston Moor, and at Anglesark in Lancashire. It is said to be used for poisoning rats, and was originally mistaken, on account of its great weight, for an ore of lead.

The metal itself is obtained by decomposing fused barium chloride by the galvanic current, or by sodium. It is a pale yellow malleable metal of sp. gr. about 4, which is easily oxidised by air, and rapidly decomposes water at common temperatures. It requires a high temperature to fuse it.

Such compounds of barium as are used in the arts are chiefly prepared from heavy spar or barium sulphate, which is remarkable for its insolubility in water and acids. In order to prepare other compounds of barium from this refractory mineral, it is ground to powder and strongly heated in contact with charcoal or some other carbonaceous substance, which removes the oxygen from the mineral in the form of carbonic oxide, and converts it into *barium sulphide*; $BaSO_4 + C_4 = 4CO + BaS$. This latter compound, being soluble in water, can be readily converted into other barytic compounds.

The artificial *barium sulphate*, which is used by painters, instead of white lead, under the name of *permanent white*, and is employed for glazing cards, is prepared by mixing the solution of barium sulphide with dilute sulphuric acid, when the barium sulphate separates as a white precipitate, which is collected, washed, and dried—

$$BaS + H_2SO_4 = H_2S + BaSO_4.$$

The artificial *barium carbonate*, which is used in the manufacture of some kinds of glass, is prepared by passing carbonic acid gas through a solution of barium sulphide, when the carbonate is precipitated; $BaS + H_2O + CO_2 = H_2S + BaCO_3$.

In preparing compounds of barium from heavy spar on the small scale, it is better to convert the sulphate into barium carbonate. 50 grs. of the finely powdered sulphate are mixed with 100 grs. of dried sodium carbonate, 600 grs. of powdered nitre, and 100 grs. of very finely powdered charcoal. The mixture is placed on a heap upon a brick or iron plate, and kindled with a match, when the heat evolved by the combustion of the charcoal in the oxygen of the nitre fuses the barium sulphate with the sodium carbonate, when they are decomposed into barium carbonate and sodium sulphate; $BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3$. The fused mass is thrown into boiling water, which dissolves the sodium sulphate and leaves the barium carbonate. The latter may be allowed to settle, and washed several times, by decantation, with distilled water, until the washings no longer yield a precipitate with barium chloride, showing that the whole of the sodium sulphate has been washed away and pure barium carbonate remains.

Baryta, BaO, may be obtained by strongly heating a mixture of barium carbonate and charcoal; $BaCO_3 + C = BaO + 2CO$. It is a heavy grey solid which combines with water with great evolution of heat to form barium hydrate.

Barium dioxide or *peroxide*, BaO_2, is obtained by heating BaO in dry air or oxygen. It is also precipitated as a crystalline aquate, $BaO_2.8Aq$. when hydric peroxide is added to solution of barium hydrate. When BaO_2 is dissolved in cold diluted acids, it yields a solution of hydric peroxide; $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.

Barium hydrate, $Ba(HO)_2$, may be prepared by passing CO_2 and steam over barium sulphide at a red heat, and decomposing the carbonate thus produced by a current of superheated steam; (1) $BaS + CO_2 + H_2O = BaCO_3 + H_2S$; (2) $BaCO_3 + H_2O = Ba(HO)_2 + CO_2$. It dissolves in boiling water, and crystallises in prisms. Crystallised barium hydrate may be procured by adding 4 oz. (or 113 grms.) of the powdered barium nitrate to 12 oz. (or 340 c.c.) of a boiling solution of sodium hydrate of sp. gr. 1.13—prepared by dissolving 3 oz. (or 85 grms.) of commercial sodium hydrate in 20 measured oz. (or 567 c.c.) of water; the solution becomes turbid from the separation of barium carbonate produced from the sodium carbonate in the hydrate; it is boiled for some minutes and then filtered; on partial cooling, some crystals of undecomposed barium nitrate are deposited, and if the clear liquid be poured off into another vessel and stirred, it deposits abundant crystals of barium hydrate having the composition $Ba(HO)_2.8Aq$; these effloresce and become opaque when exposed to air, becoming $Ba(HO)_2.Aq$; when heated to redness, they become pure barium hydrate, $Ba(HO)_2$, which fuses, but is not decomposed when further heated. The hydrate is moderately soluble in water, the solution being strongly alkaline and absorbing carbonic acid gas from the air, depositing barium carbonate.

Barium carbonate, $BaCO_3$, or Witherite, has the sp. gr. 4.3. It may be prepared by precipitating barium chloride with sodium carbonate. It is very insoluble in water, and is not decomposed by a red heat.

Barium chloride, which is the barium compound most commonly employed in the laboratory, may be obtained by dissolving the carbonate in diluted hydrochloric acid, and evaporating the solution; on cooling, the chloride is deposited in tabular crystals, $BaCl_2.2Aq$.

On the large scale, it is generally manufactured by fusing heavy spar (barium sulphate) with calcium chloride (the residue from the preparation of ammonia, see p. 124) in a reverberatory furnace, $BaSO_4 + CaCl_2 = CaSO_4 + BaCl_2$. The mass is rapidly extracted with hot water, which leaves the calcium sulphate undissolved, and the clear solution of barium chloride is decanted and evaporated. If the calcium sulphate and barium chloride were allowed to remain long together in contact with the water, barium sulphate and calcium chloride would be reproduced. This process has been improved by adding chalk and coal-dust to the mixture, when (1) $BaSO_4 + C_4 = BaS + 4CO$; (2) $BaS + CaCl_2 = BaCl_2 + CaS$. The calcium sulphide forms an insoluble compound with the lime from the chalk.

Barium chloride is easily soluble in water, but insoluble in alcohol and in strong acids. *Barium bromide* is soluble in alcohol.

Barium nitrate, $Ba(NO_3)_2$, is obtained by dissolving the carbonate in diluted nitric acid, and evaporating the solution, when octahedral crystals of the nitrate are deposited. It is an ingredient in some kinds of blasting powder used by miners. If barium nitrate be heated in a porcelain crucible, it fuses and is decomposed, leaving a grey porous mass of *baryta*;* $Ba(NO_3)_2 = BaO + 2NO_2 + O$.

Barium chlorate, $Ba(ClO_3)_2$, is employed in the manufacture of fireworks, being prepared for that purpose by dissolving the artificial barium carbonate in solution of chloric acid; it forms beautiful shining tabular crystals. When mixed with combustible substances, such as charcoal and sulphur, it imparts a brilliant green colour to the flame of the burning mixture (see p. 165).

Barium sulphate, $BaSO_4$, found as heavy spar or *cawk*, has the sp. gr. 4.5. It is precipitated whenever sulphates and barium-salts meet in solution. It is remarkable for its insolubility in water and acids, and is the form in which either barium or sulphur is determined in quantitative analysis. It dissolves in hot strong H_2SO_4, and the solution, on cooling, deposits crystals of *acid barium sulphate*, $BaH_2(SO_4)_2$.

Barium sulphide, BaS, prepared as described above, dissolves in water with decomposition, yielding barium hydrate and sulphydrate; $2BaS + 2H_2O = Ba(HO)_2 + Ba(HS)_2$. It has the property of shining in the dark after it has been exposed to the action of light.

STRONTIUM.

$Sr'' = 87.5$ parts by weight.

195. Strontium is less abundant than barium, and occurs in nature in similar forms of combination. *Strontianite*, the *strontium carbonate* ($SrCO_3$), was first discovered in the lead-mines of Strontian in Argyleshire, and has since been found in small quantity in some mineral waters.

Celestine (so called from the blue tint of many specimens†) is the *strontium sulphate* ($SrSO_4$), and is found in beautiful crystals associated with the native sulphur in Sicily. It is also met with in this country, and is the source from which the *strontium nitrate* employed in firework compositions is derived. The strontium sulphate resembles barium sulphate with respect to its insolubility, and is converted into the soluble *strontium sulphide* (SrS) by calcination with carbonaceous matter. The solution of strontium sulphide so obtained is decomposed by nitric acid, and the strontium nitrate crystallised from the solution. It has the property of imparting a magnificent crimson colour to flames, and is hence largely used for the preparation of red theatrical fire (see p. 164).

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* Containing, according to Rammelsberg, much barium peroxide.

† Said to be due to the presence of ferroso-ferric phosphate.

The metal itself is prepared in a similar manner to metallic barium,* which it much resembles, but is lighter (sp. gr. 2.54) and more fusible. It burns, when heated in air, with a crimson flame.

Strontia, SrO, resembles BaO, but does not absorb O when heated.

Strontium dioxide, SrO_2, is precipitated, in combination with water, when a solution of strontia in water is mixed with hydric peroxide.

Strontium hydrate, $Sr(HO)_2$, is made on the large scale by heating the native strontium sulphate with brown iron ore (ferric hydrate) and coal-dust. On treating the product with water, ferrous sulphide remains undissolved, and strontium hydrate passes into solution. It is used in sugar refining.

Strontium hydrate is less soluble than barium hydrate, and is converted into SrO by heat.

Strontium nitrate, $Sr(NO_3)_2$, may be prepared by dissolving strontianite in nitric acid. It crystallises from hot strong solutions in anhydrous octahedra. Cold solutions deposit prisms of $Sr(NO_3)_2.4Aq$. (Barium nitrate is always anhydrous.) Strontium nitrate is easily soluble in water, but insoluble in alcohol.

Strontium chloride, $SrCl_2$, differs from $BaCl_2$ in being deliquescent and soluble in alcohol. It crystallises in prisms, instead of tables, which are $SrCl_2.6Aq$.

Strontium sulphate, $SrSO_4$, is not so heavy as $BaSO_4$; sp. gr. 3. It is slightly soluble in water, and is easily converted into $SrCO_3$ by alkaline carbonates, in the cold, which is not the case with $BaSO_4$.

CALCIUM.

$Ca'' = 40$ parts by weight.

196. No other metal is so largely employed in a state of combination as calcium, for its oxide, lime (CaO), occupies among bases much the same position as that which sulphuric acid holds among the acids, and is used, directly or indirectly, in most of the arts and manufactures.

Like barium and strontium, it is found, though far more abundantly than these, in the mineral kingdom, in the forms of carbonate and sulphate, but it also occurs in large quantity as calcium fluoride (p. 179), and less frequently in the form of phosphate (p. 220). Calcium, moreover, is found in all animals and vegetables, and its presence in their food, in one form or other, is an essential condition of their existence.

Metallic calcium may be obtained by decomposing fused calcium iodide with metallic sodium. It has a light golden-yellow colour, is harder than lead, and very malleable; it oxidises slowly in air at the ordinary temperature, but, when heated to redness, it fuses and burns with a very brilliant white light, being converted into lime (*calx*). It decomposes water at the ordinary temperature. It is lighter than barium and strontium, its specific gravity being 1.58, and it is more easily fused.

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* Strontium has been made in quantity by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium-amalgam on a saturated solution of strontium chloride.

CARBONATE OF LIME, OR CALCIUM CARBONATE ($CaO.CO_2$ or $CaCO_3$), from which all the manufactured compounds of lime are derived, constitutes the different varieties of limestone which are met with in such abundance.

Limestones and *chalk* are simply calcium carbonate in an amorphous or uncrystallised state. The *oolite* limestone, of which the Bath and Portland building-stones are composed, is so called from its resemblance to the roe of fish (*ὠὸν, an egg*). *Marble*, in its different varieties, is an assemblage of minute crystalline grains of calcium carbonate, sometimes variegated by the presence of oxides of iron and manganese, or of bituminous matter. This last constituent gives the colour to black marble. Calcium carbonate is also found in large transparent rhombohedral crystals, which are known to mineralogists as *calcareous spar*, *calc spar*, or *Iceland spar*. When the crystals have the form of a six-sided prism, the mineral is termed *Arragonite*. The attention of the crystallographer has long been directed to these two crystalline forms of calcium carbonate, on account of the circumstance that if a prism of arragonite be heated, it breaks up into a number of minute rhombohedra of calc spar. *Satin-spar* is a variety of calcium carbonate. When slowly deposited from its solution in carbonic acid, calcium carbonate gives six-sided prisms of $CaCO_3.5Aq$.

Calcium carbonate is a chief constituent of the shells of fishes and of egg-shells, so that, except calcium phosphate, no mineral compound has so large a share in the composition of animal frames. *Corals* also consist chiefly of calcium carbonate derived from the skeletons of innumerable minute insects. The mineral *gaylussite* is a double carbonate of calcium and sodium ($CaCO_3.Na_2CO_3.5Aq$), and is scarcely affected by water unless previously heated, when water dissolves out the sodium carbonate. *Baryto-calcite* is a double carbonate of barium and calcium ($BaCO_3.CaCO_3$).

LIME (CaO).—The process by which lime is obtained from the carbonate has been already alluded to under the name of lime-burning. At a red heat calcium carbonate begins to decompose into CaO and CO_2; but unless the CO_2 be removed, it prevents further decomposition, so that marble or chalk cannot be completely decomposed in a covered crucible, and a lime-kiln must have a good draught to carry off the CO_2.

Accordingly, a kiln is commonly employed of the form of an inverted cone of brick-work (fig. 229), and into this limestone and fuel are thrown in alternate layers. The former, losing its CO_2 before it reaches the bottom of the furnace, is raked out in the form of *burnt* or *quick* lime (CaO), whilst its place is supplied by a fresh layer of limestone thrown in at the top of the kiln. Fig. 230 represents another form of kiln, in which the limestone is supported upon an arch built with large lumps of the stone above the fire, which is kept burning for about three days and nights, until the whole of the limestone is decomposed.

The usual test of the quality of the lime thus obtained consists in sprinkling it with water, with which it should eagerly combine, evolving much heat,* swelling greatly, and crumbling to a light white powder of *calcium hydrate* (*slaked lime*), $Ca(HO)_2$. Lime which behaves in this manner is termed *fat lime;* whereas, if it be found to slake feebly, it is pronounced a *poor lime*, and is known to contain considerable quantities of foreign substances, such as silica, alumina, magnesia, &c. Lime is said to be *overburnt* when it contains hard cinder-like masses of silicate of lime, formed by the combination of the silica, which is generally found in limestone, with a portion of the lime, under the influence of excessive heat in the kiln.

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* The sudden slaking of a large quantity of lime is a common cause of fire.

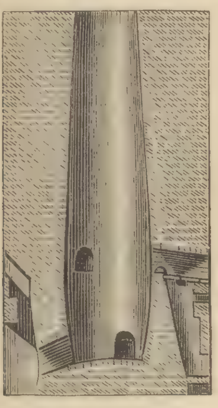

Fig. 229.—Lime-kiln.

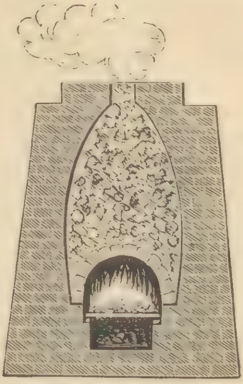

Fig. 230.—Lime-kiln.

Calcium hydrate, $Ca(HO)_2$, is much less soluble in water than barium or strontium hydrate. It requires 700 parts of cold water to dissolve it, and twice as much hot water, so that *lime-water* always gives a precipitate when boiled. The solution is strongly alkaline, and readily absorbs CO_2 from the air, which precipitates $CaCO_3$.

When lime-water is evaporated *in vacuo* over H_2SO_4, it deposits small crystals of $Ca(HO)_2$.

$Ca(OH)_2$ is easily converted into CaO by heat.

Calcium hydrate is used in manufacturing chemistry as the cheapest alkaline substance.

For the applications of lime in *mortars* and *cements*, see *Chemistry of building materials*, section 307.

Calcium dioxide, CaO_2, is precipitated in combination with $8H_2O$, when solution of sodium peroxide is added to a calcium salt.

Calcium nitrate, $Ca(NO_3)_2$, differs from those of Ba and Sr by being deliquescent, much more soluble in water, and soluble in alcohol. It crystallises with 4Aq. It occurs in well-waters and in soils, the NO_3 having been formed by oxidation of NH_3.

SULPHATE OF LIME, or CALCIUM SULPHATE, in combination with water ($CaSO_4.2H_2O$), is met with in nature, both in the form of transparent prisms of *selenite*, and in opaque and semi-opaque masses known as *alabaster* and *gypsum*. It is this latter form which yields *plaster of Paris*, for when heated to between 300° and 400° F. (or 150° and 200° C.) it loses about two-thirds of its water, becoming $3CaSO_4.2H_2O$, and if the mass be then powdered, and again mixed with water, the powder recombines with it to form a mass, the hardness of which nearly equals that of the original gypsum.

In the preparation of plaster of Paris, a number of large lumps of gypsum are built up into a series of arches, upon which the rest of the gypsum is supported; under these arches the fuel is burnt, and its flame is allowed to traverse the gypsum, care being taken that the temperature does not rise too high, or the gypsum is *overburnt*, and does not exhibit the property of recombining with water. When the operation is supposed to be completed, the lumps are carefully sorted, and those which appear to have been properly calcined are ground to a very fine powder. When this powder is mixed with water to a cream, and poured into a mould, the minute particles of calcium sulphate combine with water to reproduce the original gypsum ($CaSO_4.2H_2O$), and this act of combination is attended with a slight expansion which forces the plaster into the finest lines of the mould. If the setting of plaster of Paris be watched with the microscope, the gradual crystallisation may be perceived. The *overburnt* plaster will not crystallise unless mixed with good plaster, when the crystallisation pervades both. An addition of one-tenth of lime to the plaster hardens it and accelerates the setting.

Stucco consists of plaster of Paris (occasionally coloured) mixed with a solution of size; certain cements used for building purposes (*Keene's* and *Keating's cements*) are prepared from burnt gypsum, which has been soaked in a solution of alum and again burnt; and although the plaster thus obtained takes much longer to set than the ordinary kind, it is much harder, and therefore takes a good polish. Plaster of Paris is much damaged by long exposure to moist air, from which it regains a portion of its water, and its property of setting is so far diminished. Precipitated calcium sulphate is used by paper-makers under the name of *pearl hardener*.

$CaSO_4$ forms the mineral *anhydrite*, a bed of which, when exposed to the air in a railway cutting, has been known to increase in bulk by absorbing water to such an extent as to disturb the stability of the sides of the cutting. Calcium sulphate is contained in most natural waters, and is one of the chief causes of the *permanent hardness* which is not removed by boiling. It is much more soluble in water than strontium sulphate, so that sulphates will precipitate calcium only from strong solutions. The aqueous solution of $CaSO_4$ precipitates barium-salts immediately, but strontium-salts only after an interval, on account of the greater solubility of $SrSO_4$. The calcium sulphate is more soluble in water at 35° C. than at any other temperature, 1 part of $CaSO_4$ then dissolving in about 400 parts of water. It is insoluble in alcohol. Boiling HCl dissolves it, and deposits it in needles on cooling.

Calcium chloride ($CaCl_2$) has been mentioned as the residue left in the preparation of ammonia. The pure salt may be obtained by dissolving pure calcium carbonate (*Iceland spar*) in hydrochloric acid, and evaporating the solution, when prismatic crystals of the composition $CaCl_2.6Aq$ are obtained, which dissolve in one-fourth of their weight of cold water. When these are heated they melt at 29° C., and at about 200° C. are converted into a white porous mass of $CaCl_2.2Aq$, which is much used for drying gases. At a higher temperature, fused calcium chloride, free from water, is left; this is very useful for removing water from some liquids. When heated in air, it evolves chlorine and becomes alkaline. A saturated solution of calcium chloride boils at 355° F. (180° C.), and is sometimes used as a convenient bath for obtaining a temperature above the boiling point of water. In consequence of the attraction of calcium chloride for water, surfaces wetted with a solution of the salt never get dry. Rope mantlets, for the protection of gunners, are saturated with it to prevent their taking fire. Calcium chloride is easily soluble in alcohol.

When calcium hydrate is boiled with a strong solution of calcium chloride, it is dissolved, and the filtered solution deposits prismatic crystals of *calcium oxychloride*, $CaCl_2.3CaO.15Aq$, which are decomposed by water.

Chloride of lime; see p. 160.

Calcium fluoride, CaF_2, already described as *fluor spar* (p. 179), occurs in the bones and teeth. Many specimens of it decrepitate and emit a phosphorescent light when heated. It fuses at a red heat, and is used in metallurgy as a flux, since it attacks silicates at a high temperature. Calcium fluoride is slightly soluble in hot HCl, and is reprecipitated by NH_3. It is obtained as a gelatinous precipitate insoluble in acetic acid when $CaCl_2$ is added to an alkaline fluoride.

Calcium sulphide (CaS) has lately acquired some importance, on account of its presence in *Balmain's luminous paint.* Its property of shining in the dark after the exposure to a bright light was observed by Canton in 1761; his so-called *phosphorus* was obtained by strongly heating oyster-shells with sulphur. The phosphorescence is not due to slow oxidation, since a specimen which has been kept for more than a century in a sealed tube still exhibits it.

When CaO is acted on by H_2S, it yields a crystalline *calcium di-hydrosulphide*, $Ca(HS)_2$. When this is heated in H_2S, it is decomposed; $Ca(HS)_2 = CaS + H_2S$. The CaS is a white solid, soluble in water. When $Ca(HS)_2$ is exposed to air, it deliquesces, evolves H_2S, and becomes $Ca(HS)(HO)$; $Ca(HS)_2 + H_2O = H_2S + Ca(HS)(HO)$. Calcium sulphide occurs, combined with CaO, in the *tank-waste* of the alkali-works.

Calcium phosphate, $Ca_3(PO_4)_2$, occurs in the minerals *apatite*, *phosphorite*, *sombrerite*, and *coprolite;* in the two first it is combined with calcium fluoride, forming $3Ca_3(PO_4)_2.CaF_2$, and this is also contained in bone-ash, of which $Ca_3(PO_4)_2$ forms the larger proportion (80 per cent.). This is sold as a *non-mercurial plate powder*, under the name of *white rouge.* Calcium phosphate is nearly insoluble in water, but it is dissolved by HCl or HNO_3, and is precipitated again by ammonia. When $CaCl_2$ is added to Na_2HPO_4, a gelatinous precipitate is obtained, which becomes crystalline after a short time. The gelatinous precipitate dissolves easily in acetic acid, but the crystalline precipitate does not, and if the solution of the gelatinous precipitate in very little acetic acid be allowed to stand, or briskly stirred, it deposits crystals of $CaHPO_4.2Aq$. This salt is found in calculi in the sturgeon.

Tetra-hydrocalcic phosphate, $H_4Ca(PO_4)_2$, commonly called *superphosphate of lime*, is made by decomposing bone-ash with sulphuric acid; $Ca_3(PO_4)_2 + 2H_2SO_4 = H_4Ca(PO_4)_2 + 2CaSO_4$; the calcium sulphate is filtered off, and the superphosphate is left in solution. The pure superphosphate may be prepared by dissolving bone-ash in HCl, precipitating with ammonia, and digesting the washed precipitate of $Ca_3(PO_4)_2$ with H_3PO_4; $Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$. On allowing the solution to evaporate spontaneously, the salt crystallises in rhomboidal plates containing a molecule of water. It is dissolved by a small quantity of water, but it is decomposed and precipitated by much water, or by boiling; $CaH_4(PO_4)_2 = H_3PO_4 + CaHPO_4$. The commercial superphosphate manure, prepared by decomposing ground bones with sulphuric acid, is valued by the agriculturist for the large amount of soluble phosphate which it contains. In course of time, the proportion of soluble phosphate is found to have decreased, and the phosphate is said to have *reverted* to the insoluble form; one reason assigned for this is the action of the superphosphate upon some undecomposed tricalcic diphosphate remaining in the compound, resulting in the formation of the insoluble hydrocalcium phosphate—

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4.$$

Another cause for this *retrogression* of the superphosphate which has been prepared from mineral phosphates, is the presence of aluminium, magnesium, and iron, which gradually convert the phosphoric acid into insoluble forms.

Calcium pyrophosphate, $Ca_2P_2O_7$, when exposed for several hours to a dull red heat, forms a perfectly transparent glass of sp. gr. 2.6, which may be worked into prisms and lenses like ordinary glass, its refractive power being equal to that of crown glass. It is not acted on by acids in the cold, and even resists hydrofluoric acid.

Calcium ammonium arsenate, $CaNH_4AsO_4.7Aq$, is obtained as a white precipitate by mixing $CaCl_2$ with excess of NH_3, and adding arsenic acid. The precipitate is gelatinous at first, but changes rapidly into fine needles, especially if stirred. It is slightly soluble in water, but almost insoluble in ammonia. Dried *in vacuo*, over sulphuric acid, it becomes $Ca_3NH_4H_2(AsO_4)_3.3Aq$. Dried at 100°, it has the formula $Ca_6NH_4H_5(AsO_4)_6.3Aq$. Heated to redness, it becomes *calcium pyro-arsenate*, $Ca_2As_2O_7$.

Calcium ortho-arsenate, $Ca_3(AsO_4)_2$, and *metarsenate*, $Ca(AsO_3)_2$, have also been obtained.

Calcium silicates are found, associated with silicates of other metals, in many minerals. They also enter into the composition of most glasses. Window glass contains the silicates of calcium and sodium. Bohemian glass contains silicates of calcium and potassium.

197. *General review of the metals of the alkaline earths.*—Barium, strontium, and calcium form a highly interesting natural group of metals related to each other in a most remarkable manner. They exhibit a marked gradation in their attraction for oxygen; barium is more readily tarnished or oxidised, even in dry air, than strontium, and strontium more readily than calcium. The hydrates of the metals exhibit a similar gradation in properties; barium hydrate does not lose water, however strongly it may be heated, whereas the hydrates of strontium and calcium are decomposed at a red heat. Then barium hydrate and strontium hydrate are far more soluble in water than calcium hydrate, and all these three exhibit a very decided alkaline reaction which entitles them to the name of *alkaline earths*.

Among the other compounds of these metals, the sulphates may be named as presenting a gradation of a similar description; for barium sulphate may be said to be insoluble in water, strontium sulphate dissolves to a very slight extent, and calcium sulphate is much more soluble.

The manner in which these metals are associated in nature is also not without its significance: for if two of them are found in the same mineral, they will usually be those which stand next to each other in the group; thus strontium carbonate is found together with barium carbonate in witherite, whilst calcium carbonate is associated with strontium sulphate in celestine. Again, strontium carbonate is often found with calcium carbonate in arragonite.

198. *Relation between specific heats and atomic weights—Atomic heats.*—Since the specific gravities of the vapours of the metals of the first and second groups have not been exactly ascertained, recourse is had to their specific heats in order to ascertain their atomic weights. It will be remembered that the specific heat of a substance is the quantity of heat required to raise it 1° in temperature, as compared with the quantity of heat required to raise an equal weight of water 1°; or, more concisely, the quantity of heat required to raise one part by weight of the substance 1° (referred to water as the unit).

Thus, the specific heats of potassium, sodium, and lithium are, respectively, 0.1696, 0.2934, and 0.9408; these numbers representing the relative quantities of heat required to raise one part by weight of each of these metals 1° in temperature, supposing that an equal weight of water would be raised 1° by a quantity of heat expressed by *one*. No simple relation can be traced between these numbers, but if the quantities of heat be calculated which are required to raise *atomic* weights of these elements 1°, the case will be different.

If 0.1696 be the quantity of heat required to raise one part by weight of potassium 1°; 0.1696×39, or 6.61, will represent the quantity of heat required to raise 39 parts (1 atom) of potassium 1°. In the same way, 0.2934×23, or 6·75, is the quantity of heat required to raise 23 parts (1 atom) of sodium 1°; and 0.9408×7, or 6.59, is the quantity required to raise 7 parts (1 atom) of lithium 1°. Allowing for experimental error in the determination of the specific heats, these numbers, 6.61, 6.75, and 6.59, may be regarded as representing the same quantities of heat, and they are the *atomic heats* of these metals, that is, the relative quantities of heat required to raise an atom of each 1° in temperature.

The atomic heat, therefore, which is common to these three metals may be represented by the mean of the three numbers, or 6.65.

The experiments which have been made to determine the specific heats of those elements which can be obtained in a similar physical condition, lend strong support to the belief that the atomic heats of all elements belonging to the same group are identical, and even hold out a prospect of the identity of the atomic heats of a great majority of the elementary bodies.

A similar relation has been observed between the atomic heats of compound bodies belonging to the same group; thus, if the specific heats of the chlorides of potassium, sodium, and lithium be multiplied by the atomic weights of those chlorides, the product in each case will approach very nearly to the number 12.69. If these chlorides be allowed to contain one atom of each of their constituents, and it be supposed that the atomic heats of these constituents are identical, the half of this number (or 6.34) should represent the atomic heat of the alkali-metals, and, in fact, it does nearly coincide with that number.

The specific heat of calcium is 0.167, which, multiplied by the atomic weight of calcium (40) gives 6.68 for the atomic heat.

The specific heats of barium and strontium have not been determined, and therefore their atomic heats cannot be directly ascertained.

The specific heats of the chlorides of barium, strontium, and calcium have been ascertained to be represented by the numbers 0.09, 0.118, and 0.1686 respectively. Now, the atomic heats of the chlorides, obtained by multiplying their atomic weights into their specific heats, would be expressed by the mean number 18.72; dividing this by 3, the presumed number of atoms in the chloride, we obtain the number 6.24 for the atomic heat of each of the elements, which agrees very well with that calculated for the alkali-metals.

MAGNESIUM.

Mg' = 24.3 parts by weight.

199. Magnesium is found, like calcium, though less abundantly, in each of the three natural kingdoms. Among minerals containing this metal, those with which we are most familiar are certain combinations of silica and magnesia (silicates of magnesium) known by the names of *talc*, *steatite* or *French chalk*, *asbestos*, and *meerschaum*, which always contains water. *Magnesite* is a carbonate of magnesium. Most of the minerals containing magnesium have a remarkably soapy feel. The compounds of magnesium, which are employed in medicine, are derived either from the mineral *dolomite* or *magnesian limestone* which contains the carbonates of magnesium and calcium, or from the magnesium sulphate which is obtained from sea water and from the waters of many mineral springs.

Metallic magnesium has acquired some importance during the last few years as a source of light. When the extremity of a wire of this metal is heated in a flame, it takes fire, and burns with a dazzling white light, becoming converted into magnesia (MgO). If the burning wire be plunged into a bottle of oxygen, the combustion is still more brilliant. The light emitted by burning magnesium is capable of inducing chemical changes similar to those caused by sunlight, a circumstance turned to advantage for the production of photographic pictures by night. Attempts have been made to introduce magnesium as an illuminating agent for general purposes, but the large quantity of solid magnesia produced in its combustion forms a very serious obstacle to its use. The metal is extracted from magnesium chloride by fusing it with sodium, using sodium chloride and calcium fluoride to promote the fusibility of the mass.

On a small scale, magnesium may be prepared by mixing 900 grs. of magnesium chloride with 150 grs. of calcium fluoride, 150 of fused sodium chloride, and 150 of sodium cut into slices. The mixture is thrown into a red-hot earthen crucible, which is then covered again and heated. When the action appears to have terminated, the fused mass is stirred with an iron rod to promote the union of the globules of magnesium. It is then poured upon an iron tray, allowed to solidify, broken up, and the globules of magnesium separated from the slag; they may be collected into one globule by throwing them into a melted mixture of chlorides of magnesium and sodium and fluoride of calcium.

In most of its physical and chemical characters, magnesium resembles zinc, though its colour more nearly approaches that of silver; in ductility and malleability, it also surpasses zinc. It is nearly as light, however, as calcium, its specific gravity being 1.74. It fuses below a red heat.

and may be distilled like zinc. Cold water has scarcely any action upon magnesium; even when boiled, it oxidises the metal very slowly. In the presence of acids, however, it is rapidly oxidised by water. Solution of ammonium chloride also dissolves it, owing to the tendency of the magnesium salts to form double salts with those of ammonium; $4NH_4Cl + Mg = (NH_4)_2MgCl_4 + H_2 + 2NH_3$. Magnesium is one of the few elements which unite directly with nitrogen at a high temperature. The *magnesium nitride*, Mg_3N_2, has been obtained in transparent crystals, and is evidently composed after the type $2NH_3$, so that it is not surprising that the action of water upon it gives rise to magnesia and ammonia; $Mg_3N_2 + 3H_2O = 2NH_3 + 3MgO$.

If a foot of magnesium tape be burnt in air, the residue evolves much ammonia when boiled with water.

Magnesia, MgO, occurs, crystallised in octahedra, as the mineral *periclase*. It is prepared by decomposing magnesium carbonate by heat, and is a light white powder, very infusible, and scarcely affected by water. It dissolves easily in acids.

Magnesium hydrate, $Mg(HO)_2$, also occurs crystallised as *brucite*. When MgO is mixed with water, combination takes place, but not with much evolution of heat, as with BaO, SrO, and CaO. If excess of water be avoided, the mass *sets* like plaster of Paris. $Mg(HO)_2$ is precipitated when an alkali is added to a magnesium salt. The hydrate slowly absorbs CO_2 from the air, and is easily decomposed by heat into MgO and H_2O.

Magnesium carbonate, $MgCO_3$, is found as *magnesite*, which is imported from Greece. It is unaffected by water, and does not effervesce so briskly with acids as the other carbonates. It is easily decomposed by heat into MgO and CO_2.

When a salt of magnesium is precipitated by an alkaline carbonate, the precipitate is not the normal carbonate, as in the cases of Ba, Sr, and Ca, but a basic carbonate, or a compound of the carbonate and hydrate. Ordinary *magnesia alba*, or *light* carbonate of magnesia, is prepared by precipitating magnesium sulphate with sodium carbonate, and boiling; it generally has the composition $5MgCO_3.2Mg(HO)_2.7Aq$; $7MgSO_4 + 7Na_2CO_3 + 2H_2O = 5MgCO_3.2Mg(HO)_2 + 7Na_2SO_4 + 2CO_2$. In preparing the *heavy* carbonate, the mixed solutions are evaporated to dryness, and the sodium sulphate washed out of the residue by water. These light and heavy carbonates, when calcined, yield light and heavy magnesia, the former having 3½ times the bulk of the latter.

Magnesium carbonate, like calcium carbonate, is soluble in carbonic acid, and is present in most natural waters, causing temporary hardness, the $MgCO_3$ being precipitated by boiling.

When magnesia alba is dissolved in carbonic acid water, and the solution exposed to air, needles of $MgCO_3.3Aq$ are deposited. If this be boiled with water, it loses CO_2 and becomes a basic carbonate.

Dolomite, or *magnesian limestone*, is a mixture of magnesium carbonate and calcium carbonate in variable proportions. Magnesium carbonate is prepared from it by heating it sufficiently to decompose the $MgCO_3$, and exposing it, under pressure, to the action of water and CO_2, when the MgO is dissolved and the $CaCO_3$ is left. By passing steam through the solution, the basic magnesium carbonate is precipitated.

The *sulphate of magnesia*, or *magnesium sulphate*, so well known as

Epsom salts, is sometimes prepared by calcining dolomite to expel the carbonic acid gas, washing the residual mixture of lime and magnesia with water to remove part of the lime, and treating it with sulphuric acid, which converts the calcium and magnesium into sulphates; and since calcium sulphate is almost insoluble in water, it is readily separated from the magnesium sulphate which passes into the solution, and is obtained by evaporation in prismatic crystals, having the composition $MgSO_4.H_2O.6Aq$. Epsom salts are now made from *Kieserite*, $MgSO_4.H_2O$, found in the Stassfurt salt-beds. This is almost insoluble in water, but, when kept in contact with it, is slowly converted into $MgSO_4.7H_2O$. The preparation of Epsom salts from sea water has already been alluded to (p. 259). In some parts of Spain, magnesium sulphate is found in large quantities (like nitre in hot climates) as an efflorescence upon the surface of the soil. This sulphate, as well as that contained in well-waters, appears to have been produced by the action of the calcium sulphate, originally present in the water, upon magnesian limestone rocks; $MgCO_3 + CaSO_4 = MgSO_4 + CaCO_3$.

The crystals of magnesium sulphate fuse easily, and become $MgSO_4.H_2O$ at 150° C. The last, H_2O, can only be expelled at above 200°, and is termed the *water of constitution*.

The water of constitution in the magnesium sulphate may be displaced by the sulphate of an alkali-metal without alteration in its crystalline form; a double sulphate of magnesium and potassium ($MgSO_4.K_2SO_4.6Aq$), and a similar salt of ammonium may be thus obtained. The mineral *polyhalite* (πολύς, *many*, ἅλς, *salt*) is a remarkable salt, containing $MgSO_4.K_2SO_4.2CaSO_4.2H_2O$.* Water decomposes it into its constituent salts.

Epsom salts dissolve very easily in water, but not in alcohol. If the aqueous solution be mixed with enough alcohol to render it turbid, small oily drops separate, from which small crystals presently shoot out, and the liquid becomes, by degrees, a pasty mass of very light needles closely interlaced. These contain $7H_2O$. An aqueous solution crystallised at above 70° C. deposits $MgSO_4.H_2O.5Aq$; at 0°, crystals of $MgSO_4.H_2O.11Aq$ are formed.

Phosphates of magnesium.—$Mg_3(PO_4)_2$ is contained in bones and in some seeds. $MgHPO_4.7Aq$ is the precipitate produced by Na_2HPO_4 in magnesium salts; it is decomposed by boiling with water; $3MgHPO_4 = H_3PO_4 + Mg_3(PO_4)_2$. $MgNH_4PO_4.6Aq$ is deposited in crystals from alkaline urine, and forms *triple phosphate* calculi. It is precipitated by Na_2HPO_4 from a magnesium salt to which NH_3 has been added; $MgSO_4 + NH_3 + Na_2HPO_4 = Na_2SO_4 + MgNH_4PO_4$. Ammonium chloride should be added first to prevent the separation of $Mg(HO)_2$. The precipitation is much promoted by stirring; the $MgNH_4PO_4$ is sparingly soluble in water, and almost insoluble in ammonia; when it is heated to redness, $2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$. In quantitative analysis, Mg and P are generally determined in this form.

Magnesium-ammonium arsenate, $MgNH_4AsO_4.6H_2O$, is very similar, and is used in determining arsenic.

Magnesium borate composes the mineral *boracite*; *hydroboracite* is a hydrated borate of calcium and magnesium.

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* Polyhalite is found in the salt-beds of Stassfurt. *Kainite*, from the same locality, is $K_2SO_4.MgSO_4.MgCl_2.6Aq$.

Serpentine and *olivine* are silicates of magnesia and ferrous oxide. Some of the varieties of serpentine are employed for preparing the compounds of magnesium, for they are easily decomposed by acids with separation of silica. The minerals *asbestos*, *meerschaum*, *steatite*, and *talc* consist chiefly of magnesium silicates.

Pearl spar is a crystallised carbonate of calcium and magnesium.

Magnesium chloride is important as the source of metallic magnesium. It occurs in sea-water, in brine-springs, and in many natural waters. It is easily obtained in solution by neutralising hydrochloric acid with magnesia or its carbonate, but if this solution be evaporated in order to obtain the dry chloride, a considerable quantity of the salt is decomposed by the water at the close of the evaporation, leaving much magnesia mixed with the chloride ($MgCl_2 + H_2O = 2HCl + MgO$). This decomposition may be prevented by mixing the solution with three parts of chloride of ammonium for every part of magnesia, when a double salt, $MgCl_2.2NH_4Cl$, is formed, which may be evaporated to dryness without decomposition, and leaves fused magnesium chloride when further heated, the ammonium chloride being volatilised. The magnesium chloride absorbs moisture very rapidly from the air, and is very soluble in water. Like all the soluble salts of magnesium, it has a decidedly bitter taste. When magnesia is moistened with a strong solution of magnesium chloride, it sets into a hard mass like plaster of Paris, apparently from the formation of an oxychloride. It may be mixed with several times its weight of sand, and will bind it firmly together.

Carnallite, $KCl.MgCl_2.6Aq$, is found in crystals in the Stassfurt salt-mines. It is decomposed by water into its constituent salts. *Bischofite*, $MgCl_2.6Aq$, is found together with carnallite.

The *ammonio-magnesium* chloride, $NH_4Cl.MgCl_2.6Aq$, is not decomposed by ammonia, which therefore gives no precipitate in solutions of magnesium to which ammonium chloride has been added in sufficient quantity.

Magnesium stands apart from other metals, on the one hand, by the non-precipitation of its sulphide, and, on the other, by the tendency of all its salts, except the phosphate and arsenate, to form soluble compounds with the salts of ammonium.

ZINC.

$Zn'' = 65.5$ parts by weight = 2 vols.

200. Zinc occupies a high position among useful metals, being peculiarly fitted, on account of its lightness, for the construction of gutters, water-pipes, and roofs of buildings, and possessing for these purposes a great advantage over lead, since the specific gravity of the latter metal is about 11.5, whilst that of zinc is only 6.9. For such applications as these, where great strength is not required, zinc is preferable to iron, on account of its superior malleability; for although a bar of zinc breaks under the hammer at the ordinary temperature, it becomes so malleable at 250° F. as to admit of being rolled into thin sheets. This malleability of zinc when heated was discovered only in the commencement of this century, until which time the only use of the metal was in the manufacture of brass. When zinc is heated to 400° F., it again becomes brittle. The easy fusibility of zinc also gives it a great advantage over iron, as rendering it easy to be cast into any desired form; indeed, zinc is sur-

passed in fusibility (among the metals in ordinary use) only by tin and lead, its melting-point being below a red heat, and usually estimated at 770° F. (410° C.). Zinc is also less liable than iron to corrosion under the influence of moist air, for although a bright surface of zinc soon tarnishes when exposed to the air, it merely becomes covered with a thin film of zinc oxide (passing gradually into basic carbonate, by absorption of carbonic acid from the air) which protects the metal from further action.

The great strength of iron has been ingeniously combined with the durability of zinc, in the so-called *galvanised iron*, which is made by coating clean iron with melted zinc, thus affording a protection much needed in and around large towns, where the sulphurous and sulphuric acids arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron. The iron plates to be coated are first thoroughly cleansed by a process which will be more particularly noticed in the manufacture of tin-plate, and are then dipped into a vessel of melted zinc, the surface of which is coated with sal ammoniac (ammonium chloride) in order to dissolve the zinc oxide which forms upon the surface of the melted metal, and might adhere to the iron plate so as to prevent its becoming uniformly coated with the zinc.* A more firmly adherent coating of zinc is obtained by first depositing a thin film of tin upon the surface of the iron plate by galvanic action, and hence the name *galvanised* iron.

The ores of zinc are found pretty abundantly in England, chiefly in the Mendip Hills in Somersetshire, at Alston Moor in Cumberland, in Cornwall and Derbyshire, but the greater part of the zinc used in this country is imported from Belgium and Germany, being derived from the ores of Transylvania, Hungary, and Silesia.

Metallic zinc is never met with in nature. Its chief ores are *calamine* or zinc carbonate ($ZnCO_3$), *blende* or zinc sulphide (ZnS), and *red zinc ore*, in which zinc oxide (ZnO) is associated with the oxides of iron and manganese.

Calamine is so called from its tendency to form masses resembling a bundle of reeds (*calamus*, a reed). It is found in considerable quantities in Somersetshire, Cumberland, and Derbyshire. A compound of carbonate with hydrate of zinc, $ZnCO_3.2Zn(HO)_2$, is found abundantly in Spain. The mineral known as *electric calamine* is a silicate of zinc ($2ZnO.SiO_2.H_2O$). Blende derives its name from the German *blenden*, to dazzle, in allusion to the brilliancy of its crystals, which are generally almost black from the presence of iron sulphide, the true colour of pure zinc sulphide being white. Blende is found in Cornwall, Cumberland, Derbyshire, Wales, and the Isle of Man, and is generally associated with galena or lead sulphide, which is always carefully picked out of the ore before smelting it, since it would become converted into lead oxide, which corrodes the earthen crucibles employed in the process.

In England the extraction of zinc from its ores is carried on chiefly at Swansea, Birmingham, and Sheffield. Before extracting the metal from these ores, they are subjected to a preliminary treatment which brings them both to the condition of zinc oxide. For this purpose the calamine is simply calcined in a reverberatory furnace, in order to expel carbonic acid gas; but the blende is *roasted* for ten or twelve hours, with constant stirring, so as to expose fresh surfaces to the air, when the sulphur passes off in the form of sulphurous acid gas, and its place is taken by the oxygen, the ZnS becoming ZnO. The extraction of the metal from this zinc oxide depends upon the circumstance that zinc is capable of being distilled at a bright red heat, its boiling point being 1904° F. (1040° C.).

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* The sal ammoniac acts upon the heated zinc according to the equation, $Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$, and the zinc chloride which is formed dissolves the oxide from the surface of the metal, producing zinc oxychloride.

The facility with which this metal passes off in the form of vapour is seen when it is melted in a ladle over a brisk fire, for at a bright red heat abundance of vapour rises from it, which, taking fire in the air, burns with a brilliant greenish-white light, throwing off into the air numerous white flakes of light zinc oxide (the *philosopher's wool*, or *nil album* of the old chemists).

The distillation of zinc may be effected on the small scale in a black-lead crucible (A, fig. 231) about 5 inches high and 3 in diameter. A hole is drilled through the bottom with a round file, and into this is fitted a piece of wrought-iron gas-pipe (B) about 9 inches long and 1 inch wide, so as to reach nearly to the top of the inside of the crucible. Any crevices between the pipe and the sides of the hole are carefully stopped up with fireclay moistened with solution of borax. A few ounces of zinc are introduced into the crucible, the cover of which is then carefully cemented on with fireclay (a little borax being added to bind it together at a high temperature), and the hole in the cover is stopped up with fireclay. The crucible having been kept for several hours in a warm place, so that the clay may dry, it is placed in a cylindrical furnace with a hole at the bottom, through which the iron pipe may pass, and a lateral opening, into which is inserted an iron tube (C) connected with a forge bellows. Some lighted charcoal is thrown into the furnace, and when this has been blown into a blaze, the furnace is filled up with coke broken into small pieces. The fire is then blown till the zinc distils freely into a vessel of water placed for its reception. Four ounces of zinc may be easily distilled in half an hour.

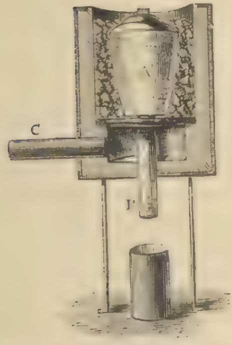

Fig. 231.—Distillation of zinc.

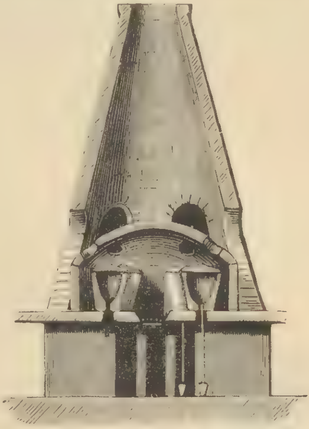

Fig. 232.—English zinc furnace.

English method of extracting zinc.—The zinc oxide, obtained as above from calamine or blende, is mixed with about half its weight of coke or anthracite coal. This mixture is introduced into large crucibles (fig. 232) with a hole in the bottom, through which passes a short wide iron pipe destined for the passage of the vapour of zinc. These crucibles are about 4 feet high by 2½ feet wide. Some large pieces of coke are first introduced into them to prevent the charge from passing into the iron pipes, and when they have been charged with the above mixture, their covers are cemented on, and they are heated in furnaces somewhat resembling those of a glass-house, each furnace receiving six crucibles, which generally contain, in all, one ton of roasted ore. When the mixture in the crucibles is heated to redness, it begins to evolve carbonic oxide produced by the combination of the carbon with the oxygen from the zinc oxide. This gas burns with a blue flame at the mouth of the iron pipe; but at a bright red heat the metallic zinc which has been thus liberated is converted into vapour, and the greenish-white flame of burning zinc is perceived at the orifice. When this is the case, about 8 feet of iron pipe are joined on to the short piece, in order to condense the vapour of zinc, which falls into a vessel placed for its reception. The distillation occupies about sixty hours, and the average yield is about 35 parts of zinc from 100 of ore, a considerable quantity of zinc being left behind in the form of zinc silicate (electric calamine), which is reduced with difficulty by distillation with carbon.

The zinc thus obtained, however, is mixed with a considerable quantity of zinc oxide, and with other foreign matters carried over from the crucibles. It is, therefore, again melted in a large iron pan, and allowed to rest, in order that the dross may rise to the surface; this is skimmed off, to be worked over again in a fresh operation, and the metal is cast into ingots, which are sent into commerce under the name of *spelter*.

Belgian process for the extraction of zinc.—At the Vieille-Montagne works, near Liége, calamine is exposed to the rain for several months in order to wash out the clay; it is then calcined to expel the water and carbonic acid gas, the zinc oxide so obtained being mixed with half its weight of coal dust, and distilled in fireclay cylinders (C, fig. 233), holding about 40 lbs. each, and set in seven tiers of six each in the same furnace, the vapour of zinc being conveyed by a short conical iron pipe (B) into a conical iron receiver (D), which is emptied every two hours into a large ladle, from which the zinc is poured into ingot moulds. Each distillation occupies about twelve hours. The advantage of this particular mode of arranging the cylinders is, that it economises fuel by allowing the poorer ores, which require less heat to distil all the zinc from them, to be introduced into the upper rows of cylinders farthest from the fire (A). There are two varieties of Belgian ore, one containing 33 and the other 46 per cent. of zinc, but a large proportion of this is in the form of silicate, which is not extracted by the distillation.

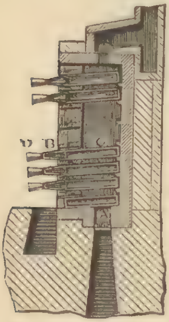

Fig. 233.—Belgian zinc furnace.

Silesian process for extracting zinc.—In Silesia the zinc oxide obtained by the calcination of calamine is mixed with fine cinders, and distilled in arched earthen retorts (A, fig. 234), into which the charge is introduced through a small door (B), which is then cemented up. The retorts are arranged in a double row in the same furnace (fig. 235), and the vapour of zinc is condensed in a bent earthenware pipe attached to each retort, and having an opening (C) near the bend, which is kept closed, unless it is necessary to clear out the pipe. In regard to the consumption of fuel, this process is far more economical than that followed in this country. The Silesian zinc is remelted, before casting into ingots, in clay instead of iron pots, since melted zinc always dissolves iron, and a very small quantity of that metal is found to injure zinc when required for rolling into sheets.

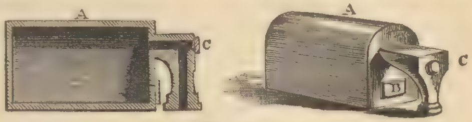

Fig. 234.

A small quantity of lead always distils over together with the zinc, and since this metal also interferes with the rolling of zinc into sheets, a portion of it is separated from zinc intended for this purpose, by melting the spelter, in large quantity, upon the hearth of a reverberatory furnace, the bed of which is inclined so as to form a deep cavity at the end nearest the chimney. The specific gravity of lead being 11.4, whilst that of zinc is 6.9, the former accumulates chiefly at the bottom of the cavity, and the ingots cast from the upper part of the melted zinc will contain but little lead, since zinc is not able to dissolve more than 1.2 per cent. of that metal.

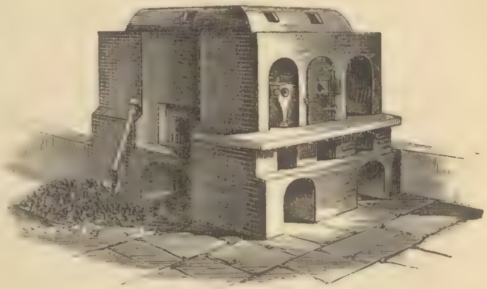

Fig. 235.—Silesian zinc furnace.

Ingots of zinc, when broken across, exhibit a beautiful crystalline fracture, which, taken in conjunction with the bluish colour of the metal, enables it to be easily identified.

The spelter of commerce is liable to contain lead, iron, tin, antimony, arsenic, copper, cadmium, magnesium, and aluminium. Belgian zinc is usually purer than the English metal.

Zinc being easily dissolved by diluted acids, it is necessary to be careful in employing this metal for culinary purposes, since its soluble salts are poisonous.

It will be remembered that the action of diluted sulphuric acid upon zinc is employed for the preparation of hydrogen. Pure zinc, however, evolves hydrogen very slowly, since it becomes covered with a number of hydrogen bubbles which protect it from further action; but if a piece of copper or platinum be made to touch the zinc beneath the acid, these metals, being electro-negative towards the zinc, will attract the electro-positive hydrogen, leaving the zinc free from bubbles and exposed on all points to the action of the acid, so that a continuous disengagement of hydrogen is maintained. As a curious illustration of this, a thin sheet of platinum or silver foil may be shown to sink in diluted sulphuric acid, until it comes in contact with a piece of zinc, when the bubbles of hydrogen bring it up to the surface. The lead, iron, &c., met with in commercial zinc, are electro-negative to the zinc, and thus serve to maintain a constant evolution of hydrogen.

Zinc also dissolves in boiling solutions of potash and soda, evolving hydrogen; $2KHO + Zn = Zn(KO)_2 + H_2$. Even solution of ammonia dissolves it slowly.

A coating of metallic zinc may be deposited upon copper by slow galvanic action, if the copper be immersed in a concentrated solution of potash, at the boiling point of water, in contact with metallic zinc, when a portion of the latter is dissolved in the form of oxide, with evolution of hydrogen, and is afterwards precipitated on the surface of the electro-negative copper.

Zinc-dust is metallic zinc which has condensed in a fine powder in smelting the ores. It is very useful in the laboratory as a reducing agent.

Zinc oxide (ZnO).—Zinc forms but one oxide, which is known in commerce as *zinc-white* or *Chinese white*, and is prepared by allowing the vapour of the metal to burn in earthen chambers through which a current of air is maintained. This zinc-white is sometimes used for painting in place of white lead (lead carbonate), over which it has the advantages of not injuring the health of the persons using it, and of being unaffected by sulphuretted hydrogen, an important consideration in manufacturing towns where that substance is so abundantly supplied to the atmosphere. Unfortunately, however, the zinc oxide does not combine with the oil of the paint as lead oxide does, and the paint is consequently more liable to peel off. The zinc oxide has the characteristic property of becoming yellow when heated, and white again as it cools. It is sometimes used in the manufacture of glass for optical purposes.

Zinc hydrate, $Zn(HO)_2$, is precipitated in a gelatinous state when caustic alkalies are added to solutions containing zinc; the precipitate dissolves in the excess of alkali, and, if this be not too great, is reprecipitated by boiling. Ammonia does not precipitate zinc hydrate from solutions containing ammonium-salts, since zinc resembles magnesium in forming double salts containing ammonium. Zinc hydrate is easily decomposed by heat; $Zn(HO)_2 = ZnO + H_2O$.

Zinc nitride, Zn_3N_2.—When zinc ethide (see *Organo-mineral compounds*) is acted on by ammonia, it is converted into *zinc-diamine*; $Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$ (*ethyle hydride*). When zinc-diamine is heated, out of contact with air, it gives zinc nitride; $3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3$. The nitride decomposes with water, evolving much heat; $Zn_3N_2 + 3H_2O = 2NH_3 + 3ZnO$.

Zinc carbonate, $ZnCO_3$, as found in nature (*calamine*, *Smithsonite*) forms rhombohedral crystals. Part of the zinc in the mineral is often replaced by isomorphous metals, such as cadmium, magnesium, and ferrous iron. $ZnCO_3$ is precipitated when zinc sulphate is boiled with hydropotassium carbonate—

$$ZnSO_4 + 2KHCO_3 = ZnCO_3 + K_2SO_4 + H_2O + CO_2.$$

The normal alkaline carbonates precipitate basic carbonates of variable composition (as is the case with magnesium). The precipitate produced by ammonium carbonate is soluble in excess.

Zinc chloride, $ZnCl_2$ (= 136.5 = 2 vols.), is prepared by dissolving Zn or ZnO in HCl, and evaporating.* If the solution contains a little

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* If iron be present, it may be separated by adding a little chlorine water to peroxidise it, and precipitating the Fe_2O_3 by adding zinc carbonate.

HCl in excess, it deposits octahedral crystals of $ZnCl_2.H_2O$. The solution, like that of $MgCl_2$, undergoes partial decomposition when evaporated, leaving an oxychloride; when this residue is distilled, $ZnCl_2$ passes over. It may also be obtained by distilling a mixture of zinc sulphate and sodium chloride. Zinc chloride is a deliquescent solid, very soluble in water, alcohol, and ether. Its attraction for water renders it a powerful caustic, and it is used as such in surgery. A strong solution of $ZnCl_2$ dissolves much ZnO, and if the solution of *oxychloride* thus formed be mixed with water, precipitates are obtained which contain Zn(OH)Cl and $Zn(OH)_2$.

Solution of $ZnCl_2$ dissolves paper and cotton, and the oxychloride dissolves wool and silk. This is sometimes useful in examining textile fabrics.

Burnett's disinfecting fluid is a solution of zinc chloride, and is capable of absorbing H_2S, NH_3, and other offensive products of putrefaction, as well as of arresting the decomposition of wood and animal substances. Zinc chloride is also used in soldering, to cleanse the metallic surface, and the careless use of this poisonous salt in soldering tins of preserved food has frequently caused accidents.

Zinc chloride is sometimes made from pyrites containing blende. This is burnt as usual to furnish SO_2 for the manufacture of sulphuric acid, when the ZnS is converted into $ZnSO_4$ which is extracted from the spent pyrites by water, and decomposed with sodium chloride, when Na_2SO_4 is deposited in crystals, leaving $ZnCl_2$ in solution.

When zinc oxide is moistened with a strong solution of zinc chloride, an oxychloride is formed, which soon sets into a hard mass, forming a very useful stopping for teeth.

Zinc sulphate, or *white vitriol*, $ZnSO_4.H_2O.6Aq$, bears a dangerous resemblance to Epsom salts, but it loses its water of crystallisation at 100° C., and is decomposed at a very high temperature into ZnO, sulphur dioxide, and oxygen, whereas $MgSO_4$ bears fusion without being decomposed. Hence $ZnSO_4$, when heated to redness, leaves a residue which is yellow when hot and white when cold.

At temperatures above 40° C. zinc sulphate crystallises as $ZnSO_4.H_2O.5Aq$, which is isomorphous with the corresponding salt of magnesium. Like the magnesium sulphate, it forms double sulphates, in which the H_2O is replaced by alkaline sulphates. $ZnSO_4.K_2SO_4.6Aq$ and $ZnSO_4.(NH_4)_2SO_4.6Aq$ are isomorphous with the Mg salts. Like all other truly isomorphous salts, the sulphates of magnesium and zinc crystallise together from their mixed solutions.

It is made on the large scale by roasting blende (zinc sulphide, ZnS) at a low red heat, when it combines with O from the air to form $ZnSO_4$, which is dissolved out by water and crystallised.

Zinc sulphide, ZnS, as found native, is usually crystallised in octahedra or dodecahedra, coloured black by ferrous sulphide. Pale yellow specimens are sometimes found. When precipitated by a soluble sulphide from a solution of a zinc salt it is perfectly white.

An intimate mixture of zinc-dust with half its weight of flowers of sulphur burns like gunpowder when kindled with a match, leaving a bulky mass of ZnS, which is primrose-yellow while hot, and white on cooling.

Zinc sulphide is insoluble in water, in alkalies, and in acetic acid, but dissolves in hydrochloric and in nitric acid. It may be sublimed in colourless crystals by strongly heating it in a current of H_2S.

Zinc silicate is found as *electric calamine*, $Zn_2SiO_4.Aq$, in rhombic crystals.

Zinc phosphate forms the mineral *hopeite*, $Zn_3(PO_4)_2.4Aq$.

Zinc differs from all the other metals in being precipitated as a white sulphide.

CADMIUM.

Cd″ = 112 parts by weight = 2 vols.

201. This metal is found in small quantities in the ores of zinc, its presence being indicated during the extraction of that metal (p. 291) by the appearance of a brown flame (*brown blaze*) at the commencement of the distillation, before the characteristic zinc flame is seen at the orifice of the iron tube. Cadmium is more easily vaporised than zinc, boiling at 1580° F. (860° C.), so that the bulk of it is found in the first portions of the distilled metal. If the mixture of cadmium and zinc be dissolved in diluted sulphuric acid, and the solution treated with hydrosulphuric acid gas, a bright yellow precipitate of *cadmium sulphide* (CdS) is obtained, which is employed in painting under the name of *cadmia*.* By dissolving this in strong hydrochloric acid and adding ammonium carbonate, cadmium carbonate ($CdCO_3$) is precipitated, from which metallic cadmium may be extracted by distillation with charcoal.

Although resembling zinc in its volatility and its chemical relations, in appearance it is much more similar to tin, and emits a crackling sound like that metal when bent. Like tin, also, it is malleable and ductile at the ordinary temperature, and becomes brittle at about 180° F. Cadmium is slightly heavier than zinc, sp. gr. 8.6. It is as fusible as tin, becoming liquid at 442° F. (228° C.), so that it is useful for making fusible alloys. An alloy of 3 parts of cadmium with 16 of bismuth, 8 of lead, and 4 of tin, fuses at 140° F. (60° C.). In its behaviour with acids and alkalies cadmium is similar to zinc, but the metal is easily distinguished from all others by its yielding a characteristic chestnut-brown oxide when heated in air. This oxide (CdO) is the only oxide of cadmium.

Cadmium chloride, $CdCl_2.2Aq$, effloresces in air, whilst zinc chloride deliquesces. Moreover, it may be dried without undergoing partial decomposition. It is fusible and volatile like zinc chloride.

Cadmium bromide, $CdBr_2.4Aq$, and the *iodide*, CdI_2, are used in photography.

Cadmium sulphate, $CdSO_4.8Aq$, is much less soluble than zinc sulphate.

Cadmium differs from all the other metals in forming a yellow sulphide insoluble in alkalies, so that its salts, mixed with excess of ammonia, and treated with H_2S, give a yellow precipitate.

GLUCINUM, OR BERYLLIUM.

Gl″ or Be″ = 9.2 parts by weight.

202. This comparatively rare metal (which derives its name from the sweet taste of its salts, γλυκύς, sweet) is found associated with silica and alumina in the *emerald*, which is a double silicate of alumina and glucina, $Al_2O_3.3SiO_2.3(GlO.SiO_2)$,

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* The darker varieties of this pigment contain thallium.

and appears to owe its colour to the presence of a minute quantity of oxide of chromium. The more common mineral *beryl*, or *aquamarine*, has a similar composition, but is of a paler green colour, apparently caused by iron. *Chrysoberyl* consists of glucina and alumina, also coloured by iron. The earlier analysts of these minerals mistook the glucina for alumina, which it resembles in forming a gelatinous precipitate on adding ammonia to its solutions, but it is a stronger base than alumina, and is therefore capable of displacing ammonia from its salts, and of being dissolved by them. Ammonium carbonate is employed to separate the glucina from alumina, since it dissolves the glucina in the cold, forming a double carbonate of glucinum and ammonium, from which the glucinum carbonate is precipitated on boiling. Glucina (GlO) is intermediate in properties between alumina and magnesia, resembling the latter in its tendency to absorb carbonic acid from the air, and to form soluble double salts with the salts of ammonium, and so much resembling alumina in the gelatinous form of its hydrate, its solubility in alkalies, and the sweet astringent taste of its salts, that it was formerly regarded as a sesquioxide like alumina. By the *radiant matter test* (p. 275), glucina phosphoresces of a bright blue colour.

The metal itself is very similar to aluminium.

ALUMINIUM.

$Al''' = 27$ parts by weight.

203. Aluminium is the representative of the class of metals usually styled *metals of the earths proper*, and including also glucinum, thorium, yttrium, zirconium, erbium, terbium, cerium, lanthanium, and didymium, but of these aluminium is the only metal having any claim to our attention on the ground of its practical importance.

Aluminium is distinguished among metals, as silicon is among non-metallic bodies, for its immense abundance in the solid mineral portion of the earth, to which, indeed, it is almost entirely confined, for it is present in vegetables and animals in so small quantity that it can scarcely be regarded as forming one of their necessary components. Church has, however, recently found it in certain cryptogamous plants, especially in the Lycopodiums; the ash of *Lycopodium alpinum* yielding one-third of its weight of alumina.

One of the oldest rocks, which appears to have originally formed the basis of the solid structure of the globe, is that known as *granite*. This mineral, which derives its name from its conspicuous *granular* structure, is a mixture, in variable proportions, of quartz, felspar, and mica, tinged of various colours by the presence of small quantities of the oxides of iron and manganese.

Quartz, which forms the translucent or transparent grains in the granite, consists simply of silica; *felspar*, the dull, cream-coloured, opaque part, is a combination of silica with oxides of aluminium and potassium, its composition being represented by the formula—

$$K_2O.3SiO_2.Al_2O_3.3SiO_2.$$

Mica, so named from the *glittering* scales which it forms in the granite, is also a double silicate of alumina and potash, but the alumina is very frequently displaced by ferric oxide, and the potash by magnesia.

By the long-continued action of air and water, the granite rock is gradually crumbled down or disintegrated, an effect which must be ascribed to a concurrence of mechanical and chemical causes. Mechanically, the rock is continually worn down by variations of temperature, by the congelation of water within its minute pores, the rock being gradually split by the expansion attendant upon such congelation.

Chemically, the action of water containing carbonic acid would tend to remove the potash from the felspar and mica in the form of carbonate of potash, whilst the silicate of alumina and the quartz would subsequently be separated by the action of water; the former, being so much lighter, would be soon washed away from the heavy quartz, and when again deposited, would constitute *clay.*

Although clay, therefore, always consists mainly of silicate of alumina, it generally contains some uncombined silicic acid, together with variable quantities of lime, of oxide of iron, &c., which give rise to the numerous varieties of clay.

Composition of Clay.

	Chinese Kaolin.	Fireclay. (Stourbridge.)	Pipeclay.
Silica	50.5	64.1	53.7
Alumina	33.7	23.1	32.0
Water	11.2	10.0	12.1
Oxide of iron	1.8	1.8	1.4
Lime	...	...	0.4
Magnesia	0.8	0.9	...
Potash Soda	1.9	...	...
	99.9	99.9	99.6

The silicate of alumina also constitutes the chief portion of several other very important mineral substances, among which may be mentioned *slate*, *fuller's earth*, and *pumice-stone*. *Marl* is clay containing a considerable quantity of carbonate of lime. *Loam* is also an impure variety of clay. The different varieties of *ochre*, as well as *umber* and *sienna*, are simply clays coloured by the oxides of iron and manganese.

Alum, which is the chief compound of aluminium employed in the arts, is always obtained either from clay or slate, but there are several processes by which it may be manufactured.

The simplest process is that in which pipeclay, or some other clay containing very little iron, is calcined, ground to powder, and heated on the hearth of a reverberatory furnace with half its weight of sulphuric acid, until it becomes a stiff paste, which is then exposed to air for several weeks. During this time the alumina of the clay is acted on by the sulphuric acid to form aluminium sulphate, which may be obtained by washing the mass with water, when the sulphate dissolves, and the undissolved silica (still retaining a portion of the alumina) is left. When the solution containing the aluminium sulphate is evaporated to a syrupy consistence and allowed to cool, it solidifies into a white crystalline mass, which is used by dyers under the erroneous name of *concentrated alum*, or *cake-alum*, and contains about 47.5 per cent. of the dry salt. The aluminium sulphate can be obtained in crystals containing $Al_23SO_4.18Aq$,* but there is considerable difficulty in obtaining these crystals on account of the extreme solubility of the salt. It is on account of this circumstance that the aluminium sulphate is usually converted into alum, which admits of very easy crystallisation and purification. In order to transform the sulphate into alum, its solution is mixed with potassium sulphate, when, by suitable evaporation, beautiful octahedral crystals are obtained, having the composition $AlK(SO_4)_2.12Aq$.

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* The mineral *alunogen* found in New South Wales has this composition (Liversidge). It forms fibrous masses like satin-spar, and occurs in sandstone rocks.

Alum is more commonly prepared from the mineral termed *alum shale*, which contains silicate of alumina, together with a considerable quantity of finely divided iron pyrites and some bituminous matter. This shale is coarsely broken up, and built into long pyramidal heaps, together with alternate layers of coal, unless the shale should happen to contain a sufficient amount of bitumen. These heaps are set fire to in several places, and are partly smothered with spent ore in order to prevent too great a rise of temperature. During this slow roasting of the heap, the iron pyrites (FeS_2) loses half its sulphur, which is converted by burning into sulphurous acid gas (SO_2), and this, in contact with the porous shale and the atmospheric oxygen, becomes converted into SO_3 (p. 208). This latter combines with the alumina to produce sulphate of alumina. The roasted heap is then allowed to remain for some months exposed to the air, and moistened from time to time, in order to promote the absorption of oxygen by the sulphide of iron (FeS), and its conversion into sulphate of iron ($FeSO_4$). The heap is afterwards lixiviated with water, which dissolves out the sulphates of aluminium and iron, together with some magnesium sulphate, which has also been formed in the process. When this *crude alum liquor* is evaporated to a certain extent, a large quantity of ferrous sulphate (green vitriol) crystallises out, and the liquid from which these crystals have separated is then mixed with so much solution of potassium chloride as a preliminary experiment has shown to be necessary to yield the largest amount of alum. The potassium chloride is obtained either from Stassfurt, or as soap-boiler's waste, or as the refuse from saltpetre refineries and glass-houses. The ferrous sulphate still left in the solution is decomposed by the potassium chloride, yielding ferrous chloride, and potassium sulphate, which combines with the aluminium sulphate to form alum; (1) $FeSO_4 + 2KCl = K_2SO_4 + FeCl_2$; (2) $K_2SO_4 + Al_2(SO_4)_3 = 2KAl(SO_4)_2$. The hot liquor is stirred while cooling, when *alum meal* is deposited in small crystals, and the $FeCl_2$ remains in solution. The alum is redissolved in boiling water, and crystallised in barrels, which are taken to pieces to get out the large crystals. If there be much magnesium sulphate in the liquor, it is subsequently obtained in crystals and sent into the market.

Where ammonium sulphate can be obtained at a cheap rate (as in the neighbourhood of gas-works), it is very commonly substituted for the potassium chloride, when *ammonia-alum* is obtained instead of *potash-alum*. The former is similar in all respects to the latter salt, except that it contains the hypothetical metal ammonium (NH_4) in place of potassium, and its formula is, therefore, $AlNH_4(SO_4)_2.12Aq$.

For all the uses of alum, in dyeing and calico-printing, in paper-making, and in the manufacture of colours, ammonia-alum answers quite as well as potash-alum, and hence both these salts are sold under the common name of alum.

These alums are the representatives of an important class of double sulphates, containing a monatomic and a triatomic metal. They all contain 12 molecules of water of crystallisation, and their crystalline form is that of the cube or octahedron. Alum dissolves in one-third of its weight of boiling water, and in seven parts of cold water; it is insoluble in alcohol. When heated, it fuses and swells up to a light porous mass of *burnt alum*, having lost its water.

The solution of alum is acid to test-papers. When solution of sodium carbonate is added to it by degrees, a precipitate of aluminium hydrate is formed, which, at first, is redissolved on stirring. The solution, to which sodium carbonate has been added as long as the precipitate redissolves, is used under the name of *basic alum* in dyeing, because stuffs immersed in it become impregnated with alumina, which serves as a mordant to attract and fix the colouring-matter when the stuff is transferred to a dye-bath.

Aluminium sulphate is superseding alum in many applications; being prepared by treating clay or Bauxite (see p. 301) with sulphuric acid, and precipitating the iron either as ferric arsenate or as Prussian blue.

Alumina.—When ammonia-alum is strongly heated it leaves a white insoluble earthy substance which is alumina itself (Al_2O_3), and differs widely from the metallic oxides which have been hitherto considered, by the feebly basic character which it exhibits.* Not only is alumina destitute of alkaline properties, but it is not even capable of entirely neutralising the acids, and hence both aluminium sulphate and alum are exceedingly acid salts.

Pure crystallised alumina is found in nature as the mineral *corundum*, distinguished by its extreme hardness, in which it ranks next to the diamond. An opaque and impure variety of corundum constitutes the very useful substance *emery*. The *ruby* and *sapphire*† consist of nearly pure alumina; *spinelle* is a compound of magnesia with alumina, $MgO.Al_2O_3$; whilst in the *topaz* the alumina is associated with silica and aluminium fluoride. In these forms the alumina is insoluble in acids, but it may be rendered soluble by fusion with acid potassium sulphate, or with alkaline hydrates. The mineral *diaspore* is a hydrate of alumina ($Al_2O_3.2H_2O$), so named from its falling to powder when heated (*διασπορά*, *dispersion*).

Aluminium hydrate, $Al_2(HO)_6$, is found crystallised as *hydrargillite*, or *Gibbsite*.

The artificially prepared aluminium hydrate is characterised by its gelatinous appearance. If a little alum be dissolved in warm water, and some ammonia added to the solution, the alumina will precipitate as a semi-transparent gelatinous mass of the hydrate $Al_2(HO)_6.2H_2O$. It is nearly insoluble in ammonia, but dissolves in potash and soda. Aluminium hydrate may be obtained in solution in water by dissolving it in solution of Al_2Cl_6, and dialysing (see p. 114). It resembles solution of silicic acid in being very easily gelatinised. When washed and dried, the gelatinous hydrate shrinks very much, and forms a mass resembling gum. The hydrate has a great attraction for most colouring-matters, with which it forms insoluble compounds called *lakes*. Thus, if a solution of alum be mixed with infusion of *logwood*, and a little ammonia added, the aluminium hydrate will form with the colouring-matter, a purplish-red *lake*, which may be filtered off, leaving the solution colourless. This property is turned to advantage in calico-printing, where the compounds of alumina are largely used as mordants.

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* The great absorption and disappearance of heat during the evaporation of the water and ammonia from this alum has led to its employment for filling the space between the double walls of fire-proof safes, which may become red-hot outside, whilst the inside is kept below the scorching-point of paper.

† Small crystals of alumina resembling natural sapphire have been obtained by the action of vapour of aluminium fluoride upon boric anhydride at a high temperature. By adding a little chromium fluoride, crystals similar to rubies and emeralds have been produced.

By the *radiant matter test* (p. 275) alumina phosphoresces crimson.

Aluminium chloride, Al_2Cl_6.—If the alumina obtained by calcining ammonia-alum be intimately mixed with charcoal, and strongly heated in an earthen tube or retort through which a stream of well-dried chlorine is passed, the oxygen of the alumina is abstracted by the charcoal, to form carbonic oxide, whilst the chlorine combines with the aluminium, yielding aluminium chloride, which passes off in vapour, and may be condensed, in an appropriate receiver, as a white crystalline solid; $Al_2O_3 + C_3 + Cl_6 = Al_2Cl_6 + 3CO$.

Instead of mixing the alumina with charcoal, it may be heated to redness in an earthen retort, through which the vapour of petroleum oil saturated with HCl gas is passed. Aluminium chloride is also obtained by heating clay in a mixture of hydrochloric acid gas and vapour of carbon disulphide. The silica of the clay is converted into silicon tetrachloride ($SiCl_4$). Al_2Cl_6 absorbs moisture from the air, and becomes partly decomposed into Al_2O_3 and HCl. By dissolving alumina in HCl and evaporating, needles of $Al_2Cl_6.12H_2O$ are obtained, but they are decomposed, when heated, into Al_2O_3, 6HCl, and $9H_2O$.

An impure solution of aluminium chloride is sold as a disinfectant under the name of *chloralum*.

Aluminium fluoride, Al_2F_6, occurs in *kryolite*, $6NaF.Al_2F_6$.

204. *Aluminium.*—In order to obtain this interesting metal, it is only necessary to pass the aluminium chloride in the state of vapour over heated sodium, which removes the chlorine in the form of sodium chloride, leaving the aluminium as a white malleable metal about as hard as zinc, and fusing at a somewhat lower temperature than silver. For the extraction of aluminium upon the large scale, the alumina is not prepared from alum, but from the mineral known as *Bauxite*, which contains alumina, together with peroxide of iron and silica.* This mineral is heated with soda-ash (see page 261), when carbonic acid gas escapes, and the silica and alumina combine with soda to form silicate of soda, and a soluble compound of alumina with soda, which is generally called *aluminate of soda*, and has the composition $3Na_2O.Al_2O_3$. On treating the mass with water, an insoluble silicate of alumina and soda is left, whilst the aluminate of soda is dissolved, and is obtained as an infusible mass when the solution is evaporated. This aluminate of soda is largely used by calico-printers as a mordant. To obtain alumina from it, the solution is decomposed by carbonic acid gas, which converts the sodium into carbonate, and precipitates the alumina as aluminium hydrate, $Al_2(HO)_6$. As the next step towards the preparation of aluminium, the hydrate is mixed with charcoal and common salt, made up into balls, dried, and strongly heated in earthen cylinders through which dry chlorine is passed. The carbon abstracts the oxygen from the alumina, forming carbonic oxide, whilst the aluminium combines with the chlorine and the aluminium chloride so formed unites with the sodium chloride, and distils over as the *double chloride of aluminium and sodium* ($Al_2Cl_6.2NaCl$). This salt is then mixed with one-

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* This mineral is found at Baux, near Arles, in the south of France, and in Antrim, Ireland; it contains silica 13 to 17 per cent., alumina 60 to 65, peroxide of iron 4 to 8, water 15 to 17. When mixed with about 3 per cent. of clay and 6 per cent. of graphite, it is said to form an excellent lining for steel-melting furnaces.

third of its weight of metallic sodium, and rather more kryolite as a flux, and heated in a reverberatory furnace, when the sodium combines with the chlorine of the aluminium chloride, leaving the metal to separate in a fused state beneath the melted sodium chloride, which protects it from oxidation. The aluminium may be rolled into sheets or drawn into wire. Commercial aluminium has been found to contain from 3 to 7.5 per cent. of iron. Silicon is also present in it, as much as 14 per cent. having been found in one sample.

It is less fusible than tin and zinc, but more so than silver, its fusing point being about 700° C. It cannot be converted into vapour. Like zinc, it is most easily rolled and bent between 100° and 150° C.

Aluminium is much more sonorous than most other metals. A bar of it suspended from a string, and struck with a hammer, emits a clear musical sound. It is remarkable as being the lightest metal capable of resisting the action of air even in the presence of moisture. Its specific gravity is 2.67. This lightness renders it valuable for the manufacture of small weights, such as the grain and its fractions, since these, when made of aluminium, are more than three times as large as when made of brass, and nearly nine times as large as platinum weights of the same denomination. It is also employed for ornamental purposes, for, though not so brilliant as silver, it is not blackened by sulphuretted hydrogen, which so easily affects that metal (page 195).

Another characteristic feature of aluminium is its comparative resistance to the action of nitric acid even at a boiling heat. No other metal commonly met with, except platinum and gold, is capable of resisting the action of nitric acid to the same extent. Hydrochloric acid, however, which will not attack gold and platinum, dissolves aluminium with facility, converting it into aluminium chloride, with disengagement of hydrogen; $Al_2 + 6HCl = Al_2Cl_6 + H_6$. Solutions of potash and soda also easily dissolve it, forming the so-called aluminates of those alkalies: thus, $6NaHO + Al_2 = Al_2(NaO)_6 + H_6$. Even when very strongly heated in air, aluminium is oxidised to a very slight extent, probably because the coating of alumina which is formed remains infusible and protects the metal beneath it. For a similar reason, apparently, aluminium decomposes steam slowly, even at a high temperature.

Aluminium decomposes water in the cold, if some aluminium iodide be present; hydrogen being set free and the aluminium hydrate produced.

When aluminium is fused with nine times its weight of copper, it forms an alloy very similar to gold in appearance, but almost as strong as iron. This alloy was strongly recommended to replace gold for ornamental purposes, but it does not retain its brilliancy so completely as that metal. Aluminium does not unite with mercury or with melted lead, both of which are capable of dissolving nearly all other metals.

205. *Mineral silicates of alumina.*—Many of the chemical formulæ of minerals which contain silicates of alumina associated with the silicates of other metallic oxides, are complicated, from the circumstance that a part of the aluminium is often replaced by iron, which, in the form of sesquioxide (Fe_2O_3), is isomorphous with it, and therefore capable of replacing it without altering the crystalline form and general character of the mineral. In a similar manner, the other metals present in the mineral may be exchanged for isomorphous representatives; thus, there are two well-known felspars, potash-felspar (*orthoclase*) and soda-felspar

(*albite*), having the formulæ $K_2O.Al_2O_3.6SiO_2$ and $Na_2O.Al_2O_3.6SiO_2$. These minerals are sometimes mingled in one and the same crystal (*potash-albite* or *pericline*) without bearing any definite equivalent proportion to each other; the formula of such a mineral would be written $(KNa)_2O.Al_2O_3.6SiO_2$. *Porphyry* has the same chemical composition as felspar.

Mica, again, is composed essentially of magnesia, alumina, and silica ($4MgO.Al_2O_3.4SiO_2$), but part of the magnesium is so constantly replaced by potassium and iron (as FeO), and part of the aluminium by iron (as Fe_2O_3), that the general formula for mica must be written $4[K_2MgFe]O.[AlFe]_2O_3.4SiO_2$. *Garnet* is essentially a double silicate of alumina and lime, but often contains magnesium, iron, or manganese, replacing part of the calcium, and iron replacing part of the aluminium, being written $3[CaMgFeMn]O.[AlFe]_2O_3.3SiO_2$. This mineral is sometimes formed artificially in the slag of the iron blast-furnaces. *Chlorite*, a very important variety of rock, is a double silicate of alumina and magnesia, with variations as expressed by the formula—

$$4[MgFe]O.[AlFe]_2O_3.2SiO_2.3H_2O.$$

Basalt is a felspathic rock containing crystals of *augite*—

$$4[CaMgFe]O.5SiO_2.$$

Cyanite, *kyanite*, or *disthene*, is a silicate of alumina ($Al_2O_3.SiO_2$), a crystal of which points north and south when freely suspended.

Gneiss is chemically composed like granite, but the mica is arranged in regular layers. *Trap* rock contains felspar together with *hornblende*, which consists of silicates of alumina, lime, magnesia, and oxide of iron. Hornblende is sometimes found replacing the mica in granite, forming the rock called *syenite*. *Lava*, from volcanoes, consists essentially of ferrous, calcium, and aluminium silicates; the presence of a considerable proportion of potassium and of phosphoric acid renders the soil formed by the weathering of lava very fertile.

Lapis lazuli, the valuable mineral which furnishes the natural ultramarine used in painting, consists chiefly of silica and alumina, which constitute respectively 45 and 32 per cent. of it, but there are also present 9 per cent. of soda, 6 per cent. of sulphuric acid, about 1 per cent. of sulphur, and a somewhat smaller quantity of iron, together with a variable proportion of lime. The cause of its blue colour is not understood, since neither of its predominant constituents is concerned in the production of such a colour in other cases. In consequence of the rarity of the mineral, the natural ultramarine has a very high price, but the *artificial ultramarine* is manufactured in very large quantities at a low cost, and forms a very good imitation. One of the processes for preparing it consists in heating to bright redness in a covered crucible, for three or four hours, an intimate mixture of 100 parts of pure white clay (kaolin), 100 of dried carbonate of soda, 60 of sulphur, and 12 of charcoal. This would be expected to yield a mixture of silicate of soda, aluminate of soda, and sulphide of sodium, the two first being white, and the latter yellow or brown, but the mass is found to have a *green* colour (*green ultramarine*). It is finely powdered, washed with water, dried, mixed with a fifth of its weight of sulphur, and gently roasted in a thin layer till the sulphur has burnt off, this operation being repeated, with fresh additions of sulphur, until the residue has a fine blue colour. In the opinion of some chemists, the presence of a small proportion of iron is essential to the blue colour, whilst others believe the colour to be due to sodium sulphide or thio-sulphate, or both.* Ultramarine is a very permanent colour under ordinary conditions of exposure to the air and light, but acids bleach it at once, with separation of gelatinous silica and evolution of sulphuretted hydrogen. Blue writing paper is often coloured with ultramarine, so that its colour is discharged by acids falling upon it in the laboratory. Chlorine also bleaches ultramarine. Starch is often coloured blue with this substance.

Phosphate of alumina, or *aluminium phosphate*, is found naturally in several forms. It occurs in large quantities in the West India Islands. *Turquoise* is a hydrated aluminium phosphate ($AlPO_4$), owing its colour to the presence of oxide of copper.† *Wavellite* has the composition $3Al_2O_3.2P_2O_5$. None of the earlier analysts detected the phosphoric acid in this mineral, on account of the difficulty in separating it from the alumina, so that even in comparatively modern chemical works it is described as a hydrate of alumina.

A gelatinous precipitate of $AlPO_4$ is formed when Na_2HPO_4 is added to solution of alum. It is soluble in HCl and in potash, but insoluble in acetic acid, which distinguishes it from aluminium hydrate.

The valency of aluminium is not very satisfactorily settled. The vapour densities of its compounds with methyle and ethyle (see *Organo-mineral compounds*) would class it as a triad, Al''', but the vapour density of its chloride points to the formula Al_2Cl_6, and not $AlCl_3$. This would indicate aluminium as a tetrad of which two atoms, singly linked, would give the hexad group $(Al^{iv}—Al^{iv})^{vi}$. In favour of this view it is urged that potassium-alum dried at 180° C. has the composition $K_2Al_2(SO_4)_4.H_2O$, that ammonium-alum dried at 190° C. and ammonium-iron-alum dried at 150° have corresponding formulæ; that this last alum may also be crystallised with H_2O and $3H_2O$, and since the water does not admit of being halved in any of these formulæ, the aluminum cannot be halved, so that the formula of alum crystals should be written $K_2Al_2(SO_4)_4.24H_2O$. Since chromium and iron are able to replace the aluminium in alum, the same reasoning would apply to them.

206. THORIUM is present in a rare Norwegian mineral *thorite*, where it is associated with silica, lime, magnesia, and other metallic oxides. The metal itself is similar to aluminium, but its oxide *thoria* appears to be ThO_2, and differs from alumina and glucina in being *insoluble in the alkalies* (potash, for example), though it dissolves in potassium carbonate. Moreover, the *sulphate of thorium* is sparingly soluble in hot water, so that it is precipitated on boiling its solution. Thoria is remarkable for its high specific gravity (9.4). It may be obtained by igniting precipitated thorium oxalate. It does not dissolve in HCl or HNO_3, but when the acid is expelled on the steam-bath, the residue dissolves in water to a kind of emulsion, in which acids or salts cause a curdy precipitate soluble in pure water. Ammonia produces a bulky precipitate, insoluble in acids.

Thorium chloride forms deliquescent needles, $ThCl_4.8H_2O$.

Thorium nitrate crystallises in tables, $Th(NO_3)_4.12H_2O$.

Thorium-sodium carbonate, $Th(CO_3)_2.3Na_2CO_3.12H_2O$, forms an amorphous precipitate.

207. YTTRIUM and ERBIUM are very rare metals found in *gadolinite*, a mineral silicate occurring at Ytterby in Sweden, and containing, beside these, glucinum, cerium, and iron. Their oxides *yttria* (Y_2O_3) and *erbia* (Er_2O_3) resemble thoria in being insoluble in the alkalies, but soluble in their carbonates; yttria is white, but erbia has a yellow colour. The salts of yttria and erbia are colourless.

The recent examination of the yttria extracted from samarskite and gadolinite has shown it to contain several weak basic oxides separated with much labour by taking advantage of slight differences in their basic power, which allow of their fractional precipitation, and identified by *radiant matter spectroscopy* (page 274), when nine of them may be distinguished by their phosphorescent spectra, though when tested by the *spark-spectrum* they give the bright lines formerly supposed to be due to yttrium only.

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* Heumann assigns to ultramarine the formula $2Na_2Al_2Si_2O_8.Na_2S_2$.

† False or bone turquoise is fossil ivory, owing its colour to the presence of the natural blue phosphate of iron.

Terbia is an earth very similar to yttria, with which it is associated in the mineral *Samarskite*, which also contains *erbia*, *holmia*, *ytterbia*, and *thulia*.

Ytterbium is another metal recently found in gadolinite.

Philippium has been obtained from Samarskite, together with *decipium*.

Scandium is believed to exist in the earth *scandia* found in minute proportion in gadolinite. The earth is infusible and insoluble in alkalies. The atomic weight of scandium, inferred from that of the oxide Sc_2O_3, is 44, which places it in Newland's and Mendelejeff's Table (page 252) in Group 3 between aluminium and gallium, where Mendelejeff predicted that an element would be discovered (which he named, in anticipation, *ekabor*) the oxide of which would have the properties actually found to characterise scandia.

208. LANTHANIUM (from λανθάνω, *to escape notice*) is also found in cerite, but it differs from cerium in forming only one oxide (La_2O_3), which is white in the hydrated but buff in the anhydrous state. When a mixture of nitrates of cerium and lanthanium is calcined, sesquioxide of cerium and oxide of lanthanium are left, and may be separated by treatment with nitric acid, diluted with 100 parts of water, which dissolves only the latter.

209. DIDYMIUM (δίδυμος, *twin*) is very similar to lanthanium, which is associated with it in cerite. It also forms but one oxide[*] (Di_2O_3), which is violet when hydrated, and brown when anhydrous. It is insoluble in potash. The salts of didymium are either pink or violet. Their solutions have a remarkable power of absorbing some of the rays of the spectrum, so that the spectroscope affords a very delicate test for this metal.[†]

210. ZIRCONIUM exists in the rare minerals *zircon* and *hyacinth*, in which its oxide *zirconia* (ZrO_2) is combined with silicic acid. Zirconia is somewhat similar to alumina, but it is insoluble in potash, and dissolves in potassium carbonate. Its sulphate, moreover, is decomposed by boiling with potassium sulphate, which removes part of the sulphuric acid, and precipitates basic zirconium sulphate. Metallic zirconium somewhat resembles amorphous silicon, but it decomposes water slowly at the boiling point, and has not been fused.

Zirconia, made into a paste with solution of boric acid, and strongly heated in iron moulds, yields masses which become even more brilliantly luminous than lime when heated in the flame of the oxyhydrogen blowpipe (*zirconia light*).

211. GALLIUM is found in very small quantities in certain ores of zinc, particularly in the blende from Bensberg in the Pyrenees. The roasted ore is treated with enough sulphuric acid to dissolve nearly all the zinc. The residue, containing the gallium, is dissolved in sulphuric acid, and the solution partly precipitated with sodium carbonate. The precipitate, containing all the gallium and part of the zinc, is dissolved in sulphuric acid, largely diluted and boiled, to precipitate the titanic acid. The solution is mixed with acid ammonium acetate, and treated with hydrosulphuric acid. The precipitate, containing zinc and gallium, is dissolved in sulphuric acid, and again partially precipitated with sodium carbonate, which gives a deposit rich in gallium; this is dissolved in exactly the required quantity of sulphuric acid, diluted and boiled, when basic gallium sulphate is deposited; on dissolving this in potash and decomposing the solution by the galvanic current, the gallium is deposited on the negative pole.

Gallium is a hard white metal of sp. gr. 5.9, remarkable for its low fusing point (30° C., 86° F.), so that it melts with the heat of the hand. It will remain liquid when cooled far below this temperature, but solidifies when touched with a piece of the solid metal.

It is not oxidised by dry air until heated nearly to redness, and the oxidation is then only superficial. Nitric acid scarcely acts upon it in the cold, but dissolves it on heating. Hydrochloric acid dissolves it, with evolution of hydrogen. Potash has a similar action.

Gallium sesquioxide, Ga_2O_3, left on igniting the nitrate, is white. When heated in hydrogen, a part sublimes, and the rest is converted into a bluish gray substance, which appears to be gallium oxide, GaO.

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[*] According to Frerichs, two, viz., DiO and Di_2O_3, to which Brauner has added Di_2O_5.

[†] The mineral *rhabdophane*, or *scovillite*, found in Cornwall, and formerly believed to contain zinc sulphide, has been shown by Hartley to be a hydrated phosphate of cerium, didymium, lanthanium, and yttrium, with the general formula $R'''PO_4.H_2O$. Recent researches have shown that didymium is not an elementary body, but may be separated into at least two others, which have been termed *neo-didymium* and *praseo-didymium*.

Gallium forms two chlorides, $GaCl_2$ and Ga_2Cl_6; they are very fusible, volatile, and deliquescent.

Gallium sulphate is very soluble in water; the solution deposits a basic salt when boiled. It combines with ammonium sulphate to form an alum, the solution of which is also precipitated by boiling.

Ammonia precipitates solutions of gallium, but the precipitate is more easily soluble in excess than in the case of aluminium. Ammonium sulphide gives a precipitate only if zinc be present, when the gallium is precipitated together with the zinc. Potash gives a precipitate which dissolves easily in excess. Potassium ferrocyanide produces a white precipitate.

The most delicate test for gallium is the production of two violet bands in the spectrum, when an induction-spark passes from the positive terminal of a secondary coil to the surface of the solution under examination into which the negative terminal of the coil is made to dip.

From the description of its properties, it will be seen that gallium bears considerable resemblance to aluminium. Its atomic weight is given as 69.865.

211*b*. GERMANIUM, Ge = 72.3.—This metal has been recently discovered in *argyrodite*.

It is extracted by fusing the powdered mineral with Na_2CO_3 and S, extracting with water, neutralising the solution with H_2SO_4, filtering from the precipitated sulphur and arsenic and antimony sulphides, and saturating with H_2S, which precipitates white germanium disulphide, GeS_2.

Germanium is a white brittle metal of sp. gr. 5.47. It fuses at about 900° C. and volatilises at a higher temperature. The fused metal crystallises in octahedra. It dissolves in sulphuric acid, but not in hydrochloric. Nitric acid converts it into white GeO_2.

It forms two series of compounds, the germanious and germanic.

Germanious chloride, $GeCl_2$, is formed by passing HCl over the heated metal, and is a colourless fuming liquid, boiling at 72° C.

Germanic chloride, $GeCl_4$, resulting from the direct union of its elements, is also a liquid, boiling at 86° C. It fumes in air, and is decomposed by water.

Germanious oxide, GeO, obtained by decomposing $GeCl_2$ with KHO, is a reducing agent. The dioxide, GeO_2, is formed when the metal burns in O; it is white, and sparingly soluble in water, from which it may be crystallised. It appears to be an acid oxide.

GeS_2 is obtained as a white precipitate by adding H_2S to a solution of GeO_2 in HCl or H_2SO_4. In the absence of acid it is somewhat soluble in water, and the solution evolves H_2S. GeS_2 is dissolved by the alkaline hydrosulphides. GeS is obtained in dark grey lustrous crystals, red by transmitted light, by heating GeS_2 in hydrogen. Hot solution of potash decomposes it into GeS_2, which dissolves, and germanium, which separates in minute crystals.

212. INDIUM is the name of a metal which was discovered, with the help of the spectroscope, in a specimen of blende from Freiberg, and in some calamines. Its name refers to an indigo-blue line in the spectrum. The examination of the metal is as yet imperfect, but it is white, malleable, and dissolves, like zinc and cadmium, in hydrochloric acid. Its specific gravity is 7.42. Fusing point, 176° C. Less easily converted into vapour than zinc or cadmium. Indium dissolves in HCl, forming $InCl_3$; in HNO_3, forming $In(NO_3)_3$; and in H_2SO_4, forming $In_2(SO_4)_3$, which crystallises with $9H_2O$.

Ammonia produces, in solutions of indium, a white precipitate, $In(OH)_3$; insoluble in excess. Ammonium carbonate gives a precipitate soluble in excess and reprecipitated by boiling. To extract indium from the Freiberg zinc, the metal is boiled with dilute sulphuric acid, employed in such quantity as to leave part of the zinc undissolved, together with indium and lead. The residue is dissolved in nitric acid, the lead and cadmium precipitated by hydrosulphuric acid, the latter expelled by boiling, and the oxide of indium precipitated from the solution by barium carbonate. When this precipitate is dissolved in hydrochloric acid, and excess of ammonia added, the white indium hydrate is precipitated, and may be reduced by heating in hydrogen. At a bright red heat it burns with a violet blue flame, yielding a yellow oxide of indium, In_2O_3. The atomic weight of indium is 113.4.

213. CERIUM is found in gadolinite, but more abundantly in *cerite*, which is

essentially a silicate of cerium. Phosphate of cerium (*cryptolite*) has also been found in brown apatite. The mineral *fluocerite* is Ce_2F_6, and *fluocerine* is an oxyfluoride. This metal has been employed medicinally in the form of oxalate of cerium. It forms two basic oxides: *cerous oxide*, Ce_2O_3, which forms colourless salts, and *ceric oxide*, CeO_2, which is yellow, and gives yellow or red salts. In this respect cerium more nearly resembles iron than aluminium. These oxides of cerium are insoluble in the alkalies; cerous oxide is easily precipitated from its salts by oxalic acid in the form of the oxalate mentioned above. Ceric oxide does not appear to form a corresponding chloride, but yields cerous chloride and free chlorine when heated with hydrochloric acid. Tetrafluoride of cerium, CeF_4, has been obtained.

Metallic cerium has been obtained by electrolysing cerous chloride; it resembles iron in colour and lustre, is unaltered by dry air, but becomes iridescent in moist air. It is malleable, and may be drawn into wire when hot. Its sp. gr. is about 6.7. Its fusing point is below that of silver. Cerium may be kindled in air more easily than magnesium, and burns more brightly; it gives brilliant sparks when struck with a flint. Hydrochloric acid and dilute sulphuric and nitric acids dissolve it.

214. URANIUM.—This is a rare metal never employed in the metallic state, but in the form of sesquioxide (U_2O_3) and black oxide ($2UO.U_2O_3$), for imparting yellow and black colours respectively to glass and porcelain. The chief source of these compounds is the mineral *pitch-blende*, which contains a large proportion of black oxide of uranium, together with silica, iron, copper, lead, and arsenic. In its chemical relations uranium presents some similarity to iron and manganese. It forms three distinct oxides, UO, U_2O_3, and UO_4, of which the first is decidedly basic, whilst the second is capable of acting both as an acid and a base, and the third is indifferent. The bright greenish-yellow colour of the salts of the sesquioxide of uranium is characteristic of the metal, and glass coloured with this oxide exhibits the remarkable optical effect of fluorescence in a very high degree.

The uranic salts (derived from U_2O_3) are reduced to uranous salts (derived from UO) by the action of light in the presence of organic substances.

Alkaline *per-uranates* have been obtained; the potassium salt is $K_4UO_8.10H_2O$.

The vapour-densities of the tetrachloride and tetrabromide of uranium lead to 240 (instead of 120) as the atomic weight of this metal.

IRON.

$Fe'' = 56$ parts by weight. $(Fe_2)^{vi} = 112$.

215. This most useful of all metals is one of those most widely and abundantly diffused in nature. It is to be found in nearly all forms of rock, clay, sand, and earth, its presence in these being commonly indicated by their colours, for iron is the commonest of natural mineral colouring ingredients. It is also found, though in small proportion, in plants, and in larger quantity in the bodies of animals, especially in the blood, which contains about 0.5 per cent. of iron in very intimate association with its colouring-matter.

But iron is very rarely found in the metallic state in nature, being almost invariably combined either with oxygen or sulphur.

Metallic iron is met with, however, in the *meteorites* or metallic masses, sometimes of enormous size, and of unknown origin, which occasionally fall upon the earth. Of these, iron is the chief component, but there are also generally present cobalt, nickel, chromium, manganese, copper, tin, magnesium, carbon, phosphorus, and sulphur.

The chief forms of combination in which iron is found in sufficient abundance to render them available as sources of the metal, are shown in the following table:—

Ores of Iron.

Common Name.	Chemical Name.	Composition.
Magnetic iron ore	Ferroso-ferric oxide	Fe_3O_4
Red hæmatite	Ferric oxide	Fe_2O_3
Specular iron		
Brown hæmatite	Ferric hydrate	$2Fe_2O_3{\cdot}3H_2O$
Spathic iron ore	Ferrous carbonate	$FeCO_3$
Clay iron-stone	Ferrous carbonate with clay	
Blackband	Ferrous carbonate with clay and bituminous matter	
Iron pyrites	Bisulphide of iron	FeS_2

These ores are frequently associated with extraneous minerals, some of the constituents of which are productive of injury to the quality of the iron. It is worthy of notice that scarcely one of the ores of iron is entirely free from sulphur and phosphorus, substances which will be seen to have a very serious influence on the quality of the iron extracted from them, and the presence of which increases the difficulty of obtaining the metal in a marketable condition.

The following table illustrates the general composition of the most important English ores of iron, with reference to the proportions of iron, and of those substances which materially influence the character of the iron extracted from the ore, viz., manganese (present as oxide or carbonate), phosphorus (present as phosphates), and sulphur (present as bisulphide of iron). The maximum and minimum quantities found in each ore are specified.

*British Iron Ores.**

In 100 parts.	Iron.		Oxide of Manganese, MnO.		Phosphoric Anhydride, P_2O_5.		Bisulphide of Iron (Pyrites).		No. of Samples Analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
Clay iron-stone from coal-measures	43.30	20.95	3.30	0.46	1.42	0.07	1.21	...	77
Clay iron-stone from the lias	49.17	17.34	1.30	...	5.05	...	1.60	...	12
Brown hæmatite	63.04	11.98	1.60	trace	3.17	...	0.30	...	23
Red hæmatite	69.10	47.47	1.13	trace	trace	trace	0.06	...	5
Spathic ore	49.78	13.98	12.64	1.93	0.22	...	0.11	...	6
Magnetic ore	57.01		0.14		0.10		0.07		1

From this table it will be gathered that, among the most abundant of the iron ores of this country, red hæmatite is the richest and purest, whilst the brown hæmatite often contains considerable proportions of sulphur and phosphorus, and the spathic ore, though containing little sulphur and phosphorus, often contains much manganese.

The argillaceous ores, or clay iron-stones found in the lias, contain more phosphorus than those from the coal-measures; and these latter, as a general rule, contain more sulphur (pyrites) than the former, although the maximum in the table does not show this.

Clay iron-stone is the ore from which the largest quantity of iron is extracted in England, since it is found abundantly in the coal-measures of Staffordshire, Shropshire, and South Wales; and it is a circumstance of great importance, in the economy of English iron-smelting, that the coal and limestone required in the smelting process, and even the fire-clay employed in the construction of the furnace, are found in the immediate vicinity of the ore.

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* This table has been compiled from the analyses given in Percy, "On Iron and Steel."

Blackband is the clay iron-stone found in the coal-fields of Scotland, and often contains between 20 and 30 per cent. of bituminous matter, which contributes to the economy of fuel in smelting it.

Red hæmatite (Fe_2O_3) is the most characteristic of the ores of iron, occurring in hard, shining, rounded masses, with a peculiar fibrous structure and a dark red-brown colour, whence the ore derives its name (*αἷμα, blood*). It is found in considerable quantities in Lancashire and Cornwall, but unfortunately its very compact structure is an obstacle to its being smelted alone, so that it is generally mixed with some clay iron-stone, and hence the iron obtained is not so free from sulphur and phosphorus as if it were extracted from hæmatite alone.

Red ochre is a soft variety of this ore, containing a little clay.

Brown hæmatite ($2Fe_2O_3.3H_2O$) is found at Alston Moor (Cumberland) and in Durham, but it is more abundant on the Continent, and is the source of most of the Belgian and French irons. *Pea iron ore* and *yellow ochre* are varieties of brown hæmatite. The Scotch ore, called *kidney-form clay iron-stone*, is really an ore of this class.

Specular iron ore (Fe_2O_3) (*oligist ore* or *iron-glance*), although of the same composition as red hæmatite, is very different from it in appearance, having a steel-grey colour and a brilliant metallic lustre. The island of Elba is the chief locality where this ore is found, but it also occurs in Germany, France, and Russia. The excellent quality of the iron smelted from this ore is due partly to the purity of the ore, and partly to the circumstance that charcoal, and not coal, is employed in smelting it.

Magnetic iron ore (Fe_3O_4), of which the *loadstone* is a variety, has a more granular structure, and a dark iron-grey colour. It forms mountainous masses in Sweden, and is also found in Russia and North America. It is generally smelted with charcoal, and yields an excellent iron. *Iron sand*, a peculiar heavy black sand of metallic lustre, consists in great measure of the magnetic ore, but contains a very large proportion of titanium. It is found abundantly in India, Nova Scotia, and New Zealand; but its fine state of division prevents it from being largely available as a source of iron.

Spathic iron ore ($FeCO_3$) is found in abundance in Saxony, and often contains a considerable quantity of manganese carbonate, which influences the character of the metal extracted from it.

The *oolitic iron ore*, occurring in the Northampton oolite, contains both hydrated sesquioxide and carbonate of iron, together with clay.

Iron pyrites (FeS_2) is remarkable for its yellow colour, its brilliant metallic lustre, and crystalline structure, being generally found either in distinct cubical or dodecahedral crystals, or in rounded nodules of radiated structure. It was formerly disregarded as a source of iron, on account of the difficulty of separating the sulphur; but an inferior quality of the metal has been extracted from the residue left after burning the pyrites in the manufacture of oil of vitriol (page 203), the residue being first well roasted in a lime-kiln to remove as much as possible of the sulphur.

The quantity of iron ore raised annually in this country is estimated at about 16 million tons, of which about 9 millions are clay and calcareous iron-stones (chiefly the former) from the lias formations of North Yorkshire, Lincolnshire, Northamptonshire, Oxford, and Wiltshire; 4½ millions are clay iron-stones of the coal formations in Scotland, England, and Wales; and about 2½ millions are hæmatites and spathic ores.

216. *Metallurgy of iron.*—Iron owes the high position which it occupies among useful metals to a combination of valuable qualities not met with in any other metal. Although possessing nearly twice as great *tenacity* or *strength* as the strongest of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being only 7.7, and is therefore particularly well adapted for the construction of bridges and large edifices, as well as for ships and carriages. It is the least yielding or malleable of the metals in common use, and can therefore be relied upon for affording a rigid support; and yet its ductility is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of $\frac{1}{10}$th inch in diameter is able to sustain 705 pounds, while a similar wire of copper, which stands next in order of tenacity, will not support more than 385 pounds.

Being, with the exception of platinum, the least fusible of useful metals, iron is applicable to the construction of fire-grates and furnaces. Nor are its qualifications all dependent upon its physical properties, for it not only enters into a great number of compounds which are of the utmost use in the arts, but its chemical relations to one of the non-metallic elements, carbon, are such, that the addition of a small quantity of this element converts it into *steel*, far surpassing iron in the valuable properties of hardness and elasticity; whilst a larger quantity of carbon gives rise to *cast-iron*, the greater fusibility of which permits it to be moulded into vessels and shapes which could not be produced by forging.

217. *English process of smelting clay iron-stone.*—The first step towards the extraction of the metal consists in calcining (or *roasting*) the ore, in order to expel water and carbonic acid gas. To effect this the ore is sometimes built up, together with a certain amount of small coal, into long pyramidal heaps, resting upon a foundation of large lumps of coal; blackband often contains so much bituminous matter that any other fuel is unnecessary. These heaps are kindled in several places, and allowed to burn slowly until all the fuel is consumed. This calcination has the effect of rendering the ore more porous, and better fitted for the smelting process. If the ore contained much sulphur, a part of it would be expelled by the roasting in the form of sulphurous acid gas. The $FeCO_3$ is converted into Fe_2O_3, which is less likely to combine with silica and form a fusible slag.

More commonly the calcination is effected in kilns resembling lime-kilns, and it is often altogether omitted as a separate process, the expulsion of the water and carbonic acid gas being then effected in the smelting-furnace itself as the ore descends.

The calcined ore is smelted in a huge *blast-furnace* (fig. 236) from fifty to eighty feet high, built of massive masonry, and lined internally with firebrick. Since it would be impossible to obtain a sufficiently high temperature with the natural draught of this furnace, air is forced into it at the bottom, under a pressure of three or four pounds (sometimes even ten) upon the inch, through *tuyère* or *twyer* pipes, the nozzles of which pass through apertures in three sides of the furnace.

It would be very easy to reduce to the metallic state the oxide of iron contained in the calcined ore, by simply throwing it into this furnace, together with a proper quantity of coal, coke, or charcoal; but the metallic iron fuses with so great difficulty, that it is impossible to separate it from the clay unless this latter is brought into a liquid state; and even then the fusion of the iron, which is necessary for complete separation, is only effected after it has formed a more easily fusible compound with a small proportion of carbon derived from the fuel.

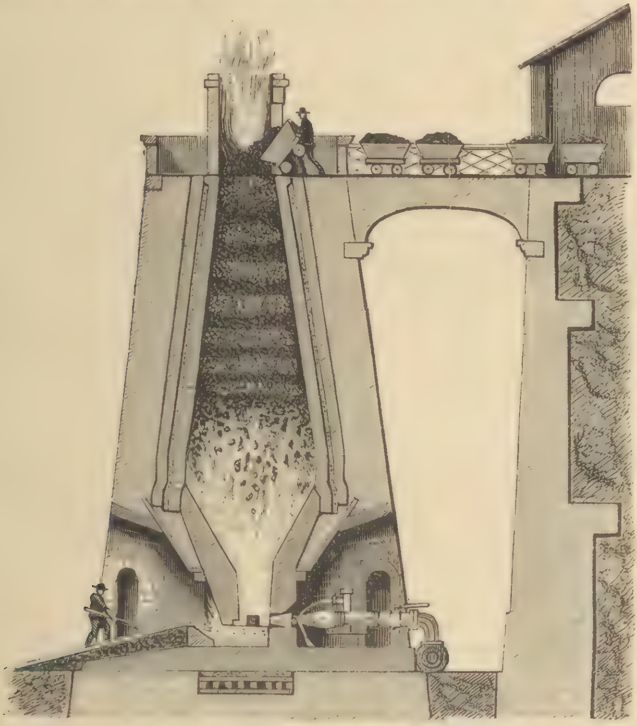

Fig. 236.—Blast-furnace for smelting iron ores.

Now, clay is even more difficult to fuse than iron, so that it is necessary to add, in the smelting of the ore, some substance capable of forming with the clay a combination which is fusible at the temperature of the furnace. If clay (silicate of alumina) be mixed with limestone (carbonate of lime), and exposed to a high temperature, carbonic acid gas is expelled from the limestone, and the lime unites with the clay, forming a double silicate of alumina and lime, which becomes perfectly liquid, and, when cool, solidifies to a glass or *slag*. The limestone is here said to act as a *flux*, because it induces the clay to *flow* in the liquid state. In order, therefore, that the clay may be readily separated from the metallic iron, the calcined ore is mixed with a certain proportion of limestone before being introduced into the furnace.

Great care is necessary in first lighting the blast-furnace lest the new masonry should be cracked by too sudden a rise of temperature, and, when once lighted, the furnace is kept in constant work for years until in want of repair. When the fire has been lighted, the furnace is filled up with coke, and as soon as this has burnt down to some distance below the chimney, a layer of the mixture of calcined ore with the requisite proportion of limestone is thrown upon it; over this there is placed another layer of coke, then a second layer of the mixture of ore and flux, and so on, in alternate layers, until the furnace has been filled up; when the layers sink down, fresh quantities of fuel, ore, and flux are added, so that the furnace is kept constantly full. As the air passes from the tuyère pipes into the bottom of the furnace, it parts with its oxygen to the carbon of the fuel, which it converts into carbonic acid gas (CO_2); the latter, passing over the red-hot fuel as it ascends in the furnace, is converted into carbonic oxide (CO) by combining with an additional quantity of carbon. It is this carbonic oxide which reduces the calcined ore to the metallic state, when it comes in contact with it, at a red heat, in the upper part of the furnace, for carbonic oxide removes the oxygen, at a high temperature, from the oxides of iron, and becomes carbonic acid gas; the iron so reduced decomposes another portion of the carbonic oxide and enters into combination with a small proportion of carbon to form cast-iron, which fuses and runs down into the *crucible* or cavity for its reception at the bottom of the furnace. The clay contained in the ore is acted upon by the lime of the flux, producing a double silicate of alumina and lime, which also falls in the liquid state into the crucible, where it forms a layer of "slag" above the heavier metal. This slag, which has five or six times the bulk of the iron, is allowed to accumulate in the crucible, and to run over its edge down the incline upon which the blast-furnace is built; but when a sufficient quantity of cast-iron has collected at the bottom of the crucible, it is run out through a hole provided for the purpose, either into channels made in a bed of sand, or into iron moulds, where it is cast into rough semi-cylindrical masses called *pigs*, whence cast-iron is also spoken of as *pig-iron*. The temperature of the furnace is, of course, highest in the immediate neighbourhood of the tuyères; the reduction of the iron to the metallic state appears to commence at about two-thirds of the way down the furnace, the volatile matters of the ore, fuel, and flux being driven off before this point is reached.

Some idea may be formed of the immense scale upon which the smelting of iron ores is carried out, when it is stated that each furnace consumes, in the course of twenty-four hours, about 50 tons of coal, 30 tons of ore, 6 tons of limestone, and 100 tons of air. The cast-iron is run off from the crucible once or twice in twelve hours, in quantities of five or six tons at a time. The average yield of calcined clay ironstone is 35 per cent. of iron.

The gases escaping from the chimney of the blast-furnace are highly inflammable, for they contain, beside the nitrogen of the air blown into the furnace, a considerable quantity of carbonic oxide and some hydrogen, together with the carbonic acid gas formed by the action of the carbonic oxide upon the ore. Since the carbonic oxide and hydrogen confer considerable heating power upon these gases, they are employed, in some iron-works, for heating steam-boilers, or for calcining the ore, or for raising the temperature of the blast.

The composition of the gas issuing from a hot-blast furnace (fed with uncoked coal) may be judged of from the following table:—

Gas from Blast-Furnace, in 100 *vols.*

Nitrogen	55.35 vols.	Carbonic acid gas	7.77 vols.
Carbonic oxide	25.97 ,,	Marsh gas	3.75 ,,
Hydrogen	6.73 ,,	Olefiant gas	0.43 ,,

The carbonic oxide, of course, renders these gases highly poisonous, and fatal accidents occasionally happen from this cause.

Although the bulk of the nitrogen present in the air escapes unchanged from the furnace, it is not improbable that a portion of it contributes to the formation of the cyanide of potassium (KCN), which is produced in the lower part of the furnace, the potassium being furnished by the ashes of the fuel.

The hot blast.—On considering the enormous quantity of air which passes through the blast-furnace, it will be seen that it occasions the loss of a considerable amount of heat. In order to economise the fuel, *hot-blast furnaces* are fed with air of which the temperature is raised to about 900° F., by passing it through heated iron pipes or over hot firebricks before allowing it to enter the blast-furnace. The higher temperature which is thus attained permits the use of uncoked coal, which would not have given enough heat in a cold-blast furnace, and the same quantity of ore may be smelted with less than half the coal formerly employed, since the blast may be heated by means of the waste heat of the furnace. It appears, however, that the *hot-blast iron* is inferior in quality to that obtained from the same ore in a cold-blast furnace, and this is generally explained by referring to the larger quantity of sulphur contained in the raw coal; to the circumstance, that the cast-iron being exposed to a much higher temperature in the hot-blast furnace is more liable to receive and retain a larger amount of foreign substances; and (most important of all) to the custom of extracting iron in a hot-blast furnace from slags obtained in the subsequent processes of the iron-manufacture, which could not be smelted in a cold-blast furnace. These slags always contain sulphur and phosphorus, and therefore yield an inferior quality of iron. Hence the distinction commonly drawn between *mine iron* extracted from the ore without admixture of slags, and *cinder iron* (or *kentledge*) in the preparation of which slag or cinder has been employed.

The *slag from the blast furnace* is essentially a glass composed of a double silicate of aluminium and calcium, the composition of which varies much according to the nature of the earthy matters in the ore, and the composition of the flux. Its colour is generally grey, streaked with blue, green, or brown.

The nature of the flux employed must, of course, be modified according to the composition of the earthy substances (or *gangue*) present in the ore. Where this consists of clay (silicate of alumina) the addition of lime (which is sometimes added in the form of limestone and sometimes as quicklime) will provide for the formation of the double silicate of alumina and lime. But if the iron-ore happened already to contain limestone, an addition of clay would be necessary, or if quartz were present, consisting of silica only, both lime and alumina (in the form of clay) will be necessary as a flux. It is sometimes found economical to employ a mixture of ores containing different kinds of gangue, so that one may serve as a flux to the other. If a proper proportion of lime were not added, a portion of the oxide of iron would combine with the silica and be carried off in the slag; but if too large a quantity of lime be employed, it will diminish the fusibility of the slag, and prevent the complete separation of the iron from the earthy matter. The most easily fusible slag which can be formed by the action of lime upon clay has the composition $6CaO.Al_2O_3.9SiO_2$; but in English furnaces, where coal and coke are employed, it is found necessary to employ a larger proportion of lime to convert the sulphur of the fuel into calcium sulphide, so that the slag commonly has a composition more nearly represented by the formula $12CaO.2Al_2O_3.9SiO_2$, which would express a compound of 6 molecules of normal calcium silicate with 1 molecule of normal aluminium silicate; $6Ca_2SiO_4.Al_4(SiO_4)_3$.

Since iron, manganese, and magnesium are commonly found occupying the place of a portion of the calcium, a more general formula for the slag from English blast-furnaces would be $6(CaFeMnMg)_2SiO_4.Al_4(SiO_4)_3$.

A fair impression of the ordinary composition of the slag from blast-furnaces is conveyed by the following table:—

Slag from Blast-Furnace; in 100 *parts.*

Silica	43.07	Oxide of manganese (MnO)	1.37
Alumina	14.85	Potash (K_2O)	1.84
Lime	28.92	Sulphide of calcium	1.90
Magnesia	5.87	Phosphoric oxide (P_2O_5)	trace
Oxide of iron (FeO)	2.35		

From 10 to 30 cwt. of slag are produced per ton of cast-iron smelted.

These slags are sometimes run from the blast-furnace into iron moulds, in which they are cast into blocks for rough building purposes. The presence of a considerable proportion of potash has led to experiments upon their employment as a manure, for which purpose they have been blown out, when liquid, into a finely divided frothy condition fit for grinding and applying to the soil. By blowing steam through the slag it is converted into a substance resembling spun glass, and used, under the name of *mineral cotton*, for packing round steam-pipes, &c.

218. CAST-IRON is, essentially, composed of iron with from 2 to 5 per cent. of carbon, but always contains other substances derived either from the ore or from the fuel employed in smelting it. On taking into consideration the energetic de-oxidising action in the blast-furnace, it is not surprising that portions of the various oxygen compounds exposed to it should part with their oxygen, and that the elements thus liberated should find their way into the cast-iron. In this way the silica is reduced, and its silicon is found in cast-iron in quantity sometimes amounting to 3 or 4 per cent. Hæmatite pig is usually rich in silicon, from the presence of silica in an easily reducible condition in the ore. Sulphur and phosphorus are also generally present in cast-iron, but in very much smaller quantity; their presence diminishes its tenacity, and the smelter endeavours to exclude them as far as possible, though a small quantity of phosphorus appears to be rather advantageous for some castings, since it augments the fusibility and fluidity of the cast-iron. The sulphur is chiefly derived from the coal or coke employed in smelting, and for this reason charcoal would be preferable to any other fuel if it could be obtained at a sufficiently cheap rate. The iron-works of America and

those of the European continent enjoy a great advantage in this respect over those of England. The phosphorus is obtained chiefly from the phosphates existing in the ore or in the flux.* It appears to exist in the iron, at least in some cases, as Fe_4P. The proportion of phosphorus taken up by the cast-iron increases with the temperature of the blast-furnace. Manganese, amounting to 1 or 2 per cent., is often met with in cast-iron, having been reduced from the oxide of manganese, which is generally found in iron ores. Other metals, such as chromium, cobalt, &c., are also occasionally present, though in such small quantities as to be of no importance in practice.

The following table exhibits the largest and smallest proportion of the various elements determined in the analysis of upwards of a hundred specimens of cast-iron :—

Composition of Cast-Iron.†

	Maximum.	Minimum.	
Carbon	4.81	1.04	per cent.
Silicon	4.77	0.08	,,
Sulphur	1.06	...	,,
Phosphorus	1.87	trace	,,
Manganese	6.08	trace	,,
Iron	...	...	,,

In order to understand the difference observed in the several varieties of cast-iron, it is necessary to consider the peculiar relations between iron and carbon. Iron fused in contact with carbon is capable of combining with nearly 6 per cent. of that element, to form a white, brilliant, and brittle compound, which may be represented pretty nearly as composed of Fe_4C. Under certain circumstances, as this compound of iron and carbon cools, a portion of the carbon separates from the iron, and remains disseminated throughout the mass in the form of minute crystalline particles very much resembling natural graphite. If a broken piece of iron containing these scales be examined, the fracture will be found to exhibit a more or less dark grey colour, due to the presence of the uncombined carbon, and for this reason a cast-iron in which a portion of the carbon has thus separated is commonly spoken of as *grey iron*, whilst that in which the whole of the carbon has remained in combination with the metal exhibits a white fracture, and is termed *white iron* or *bright iron*. Intermediate between these is the variety known as *mottled iron*, which has the appearance of a mixture of the grey and white varieties.

The different condition of the carbon in the two varieties of cast-iron is rendered apparent when the metal is dissolved in diluted sulphuric or hydrochloric acid, for any carbon which exists in the uncombined state will then be left, whilst that which had been in combination with the iron passes off in the form of peculiar compounds of carbon and hydrogen, which impart the disagreeable odour perceived in the gas evolved when the metal is dissolved in an acid.

The properties of these two varieties of cast-iron are widely different, grey iron being so soft that it may be turned in a lathe, whilst the white iron is extremely hard, and of higher specific gravity. Again, although white iron fuses at a lower temperature than grey iron, the latter is far more liquid when fused, and is therefore much better fitted for casting.

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* Phosphorus, in the form of phosphates, is sometimes found in coal.

† Compiled from Percy, "On Iron and Steel."

Although the presence of uncombined carbon is the chief point which distinguishes grey from white iron, other differences are commonly observed in the composition of the two varieties. The white iron usually contains less silicon than grey iron, but a larger proportion of sulphur. White iron also usually contains a much larger quantity of manganese.

The difference in the composition of these three varieties of cast-iron is shown in the following table:—

	Grey.	Mottled.	White.
Iron	90.24	89.31	89.86
Combined carbon . .	1.02	1.79	2.46
Graphite . . .	2.64	1.11	0.87
Silicon	3.06	2.17	1.12
Sulphur* . . .	1.14	1.48	2.52
Phosphorus . . .	0.93	1.17	0.91
Manganese . . .	0.83	1.60	2.72
	99.86	98.63	100.46

As might be expected, it is not easy to tell where a cast-iron ceases to be grey and begins to be mottled, or where the mottled iron ends and white iron begins. There are, in fact, eight varieties or *grades* of cast-iron in commerce, distinguished by the numbers one to eight, of which No. 1 is dark grey, and contains the largest proportion of graphite, which diminishes in the succeeding numbers up to No. 8, which is the whitest iron, the intermediate numbers being more or less mottled.

The particular variety of cast-iron produced is to some extent under the control of the smelter; a furnace in good order appearing usually to yield grey iron, whilst a defective furnace, or one supplied with too small a proportion of fuel, will commonly give a white iron. But the metal sometimes varies considerably at different levels in the *crucible* of the furnace, so that pigs of different degrees of greyness are obtained at the same tapping. Mottled cast-iron surpasses both the other varieties in tenacity, and is therefore preferred where this quality is particularly desirable.

The dark grey iron used for casting, known as *foundry-iron*, is produced at a higher temperature, by supplying the blast furnace with a larger proportion of fuel than is employed in making the lighter *forge-iron* destined for conversion into wrought-iron. The extra consumption of fuel, of course, renders the foundry-iron more expensive. When a furnace is worked with a low charge of fuel to produce a white iron, a larger quantity of iron is lost in the slag, sometimes amounting to 5 per cent. of the metal, whilst the average loss in producing grey iron does not exceed 2 per cent. Ores containing a large proportion of manganese are generally found to yield a white iron.

When grey iron is melted, the particles of graphite to which its grey colour is due are dissolved by the liquid iron, and if it be poured into a cold iron mould so as to solidify it as rapidly as possible, the external portion of the casting will present much of the hardness and appearance of white iron, the sudden cooling having prevented the separation of the graphite. This affords the explanation of the process of *chill-casting*, by which shot, &c., made of the soft fusible grey iron, are made to acquire, externally, a hardness approaching that of steel. It is a common practice to produce compound castings, that portion of the mould where chilling and consequent hardness is required being made of thick cast-iron, and the other part, which is to give a tougher and a softer casting, of sand. When white pig-iron is melted at an extremely high temperature (in a Siemens furnace) and slowly cooled, it becomes grey.

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* The proportion of sulphur in these samples is unusually large; it seldom exceeds 0.5 per cent. in good pig-iron.

The *specific gravity* of cast-iron varies between 6.92 (grey) and 7.53 (white), and its *fusing point* is somewhat below 3000° F.

Modern experiments throw some doubt upon the existence of carbon in a state of actual chemical combination in cast-iron. It has been found that, when acting upon mercuric chloride, white cast-iron generates considerably more heat than pure iron; this would indicate that absorption of heat had taken place in the formation of white cast-iron (which contained 4 per cent. of "combined" carbon), whereas, had the carbon combined chemically with the iron, generation of heat should have taken place. On the other hand, it was found, by the same method, that manganese and carbon do generate heat, and therefore enter into true chemical combination. This fact may have some bearing upon the use of manganese in the manufacture of steel.

CONVERSION OF CAST-IRON INTO BAR OR WROUGHT-IRON.

219. In order to convert cast-iron into bar-iron, it is necessary to reduce it as far as possible to the condition of pure iron, by removing the carbon, silicon, and other substances associated with it. This purification is effected upon the principle, that when cast-iron is strongly heated in contact with oxide of iron, its carbon is evolved in the form of carbonic oxide, whilst the silicon, also combining with the oxygen from a part of the oxide of iron, is converted into silica, which unites with another portion of the oxide to form a fusible slag easily separated from the metal.

This process is termed *puddling* when carried out by manual labour or by rotating furnaces, and *Bessemerising* when performed by forcing fine streams of air through the melted metal.

With pig-iron containing much graphite and silicon, the puddling process is preceded by the process of *refining*, which will therefore be first described.

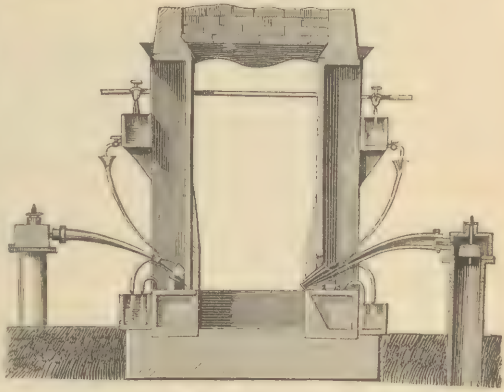
Fig. 237.—Hearth for refining pig-iron.

Refining cast-iron.—This process consists essentially in exposing the metal, in the fused state, to the action of a blast of air in which part of the oxygen has been converted into carbonic oxide by passing over red-hot coke or charcoal. The *refinery* (figs. 237, 238) is a rectangular trough with double walls of cast-iron, between which cold water is kept circulating to prevent their fusion. This trough is about 3½ feet long by 2½ wide, and usually lined with fireclay; on each side of it are arranged three tuyère pipes for the supply of air, inclined at an angle of 25° to 30° to the bottom of the furnace, which is fed with coke, unless the very best iron is required, as for the manufacture of tin-plate, when charcoal is generally used in the refinery.

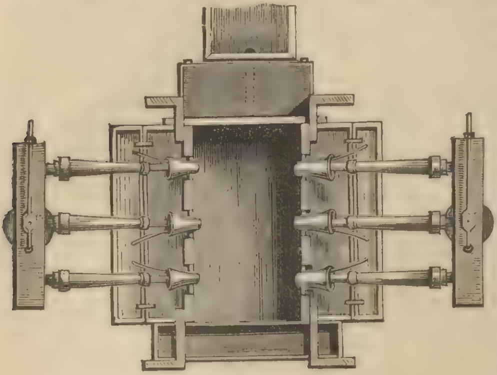
Fig. 238.—Hearth for refining pig-iron.

This furnace having been filled to a certain height with fuel, five or six pigs of iron (from 20 to 30 cwt.) are arranged symmetrically upon it, and covered with coke, a blast of air being forced in through the tuyères, under a pressure of about 3 lbs. upon the inch. In about a quarter of an hour the metal begins to fuse gradually, and to trickle down through the fuel to the bottom of the refinery, a portion of the iron being converted into oxide in its descent, by the air issuing from the tuyère pipes. When the whole of the metal has been fused, the air is still allowed to play for some time upon its surface, when the fused metal appears to boil in consequence of the escape of bubbles of carbonic oxide.

After about two hours the tap-hole is opened, and the molten metal run out into a flat cast-iron mould kept cold by water, in order to chill the metal and render it brittle. The plate of *refined iron* thus obtained is usually about 2 inches thick. The slag (or *finery cinder*) is generally received in a separate mould; its composition may be generally expressed by the formula $2FeO.SiO_2$, the silica having been derived from the silicon contained in the cast-iron.

The change effected in the composition of the iron by the process of refining will be apparent from the following table:—

Refined Iron.

Iron	95.14	Phosphorus	0.73
Carbon	3.07	Manganese	trace
Silicon	0.63	Slag	0.44
Sulphur	0.16		

The carbon, therefore, is not nearly so much diminished as the silicon, which is in some cases reduced to $\frac{1}{10}$th of its former proportion by the refining process. Half of the sulphur is also sometimes removed, being found in the slag as sulphide of iron. The phosphorus is not removed to the same extent in the refining process, though some of it is converted into ferrous phosphate, which may be found in the finery cinder.

The further purification of the metal could not be effected in the refinery, since the fusibility of the iron is so greatly diminished as it approaches to a pure state, that it could not be retained in a fluid condition at the temperature attainable in this furnace, and a more spacious hearth is required upon which the pasty metal may be kneaded into close contact with the oxide of iron which is to complete the oxidation and separation of the carbon. For this reason the metal is transferred to the puddling furnace.

The *puddling* process is carried out in a reverberatory furnace (figs. 239, 240) connected with a tall chimney provided with a damper, so as to admit of a very perfect regulation of the draught. A bridge of firebrick between the grate and the hearth prevents the contact of the coal with the iron to be puddled. The hearth is composed either of firebrick or of cast-iron plates, covered with a layer of very infusible slag, and cooled by a free circulation of air between them. This hearth is about 6 feet in length by 4 feet in the widest part near the grate, and 2 feet at the opposite end; it is slightly inclined towards the end farthest from the grate, and finishes in a very considerable slope, at the lowest point of which is the *floss-hole* for the removal of the slag. Since the metal is to attain a very high temperature in this furnace (estimated at

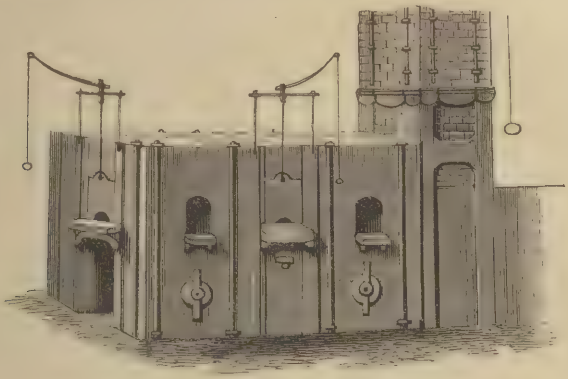

Fig. 239.—Puddling furnace.

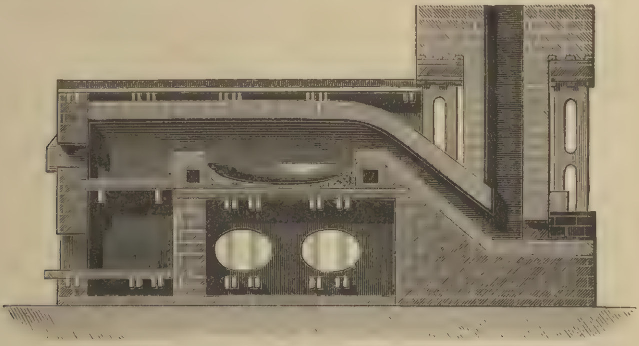

Fig. 240.—Puddling furnace.

1500° C.), it is usually covered with an iron casing, so as to prevent any entrance of cold air through chinks in the brickwork.

About 5 cwt. of the fine metal is broken up and heaped upon the hearth of this furnace, together with about 1 cwt. of iron scales (black oxide of iron, Fe_3O_4), and of *hammer-slag* (basic silicate of iron, obtained in subsequent operations), which are added in order to assist in oxidising the impurities. When the metal has fused, the mass is well stirred or puddled so that the oxide of iron may be brought into contact with every part of the metal, to effect the oxidation of the impurities. The metal now appears to boil, in consequence of the escape of carbonic oxide, and in about an hour from the commencement of the puddling, so much of the carbon has been removed that the fusibility of the metal is considerably diminished, and instead of retaining a fused condition at the temperature prevailing in the furnace, it assumes a granular, *sandy* or *dry* state, spongy masses of pure iron separating or *coming to nature* in the fused mass. The puddling of the iron is continued until the whole has assumed this granular appearance, when the evolution of carbonic oxide ceases almost entirely, showing that the removal of the carbon is nearly completed. The damper is now gradually raised so as to increase the temperature and soften the particles of iron, in order that they may be collected into a mass; and, the more easily to effect this, a part of the slag is run off through the floss-hole. The workman then collects some of the iron upon the end of the paddle, and rolls it about on the hearth until he has collected a sort of rough ball of iron, weighing about half a hundredweight. When all the iron has been collected into balls in this way, they are placed in the hottest part of the furnace, and pressed occasionally with the paddle, so as to squeeze out a portion of the slag with which their interstices are filled. The doors are then closed to raise the interior of the furnace to a very high temperature, and after a short time, when the balls are sufficiently heated, they are removed from the furnace, and placed under a steam hammer, which squeezes out the liquid slag, and forces the softened particles of iron to cohere into a continuous oblong mass or *bloom*, which is then passed between rollers, by which it is extended into bars. These bars, however (*Rough* or *Puddled*, or *No. 1 Bar*), are always hard and brittle, and are only fit for such constructions as railway bars, where hardness is required rather than great tenacity. In order to improve this latter quality, the rough bars are cut up into short lengths, which are made into bundles, and, after being raised to a high temperature in the *mill-furnace*, are passed through rollers, which weld the several bars into one compound bar, to be subsequently passed through other rollers until it has acquired the desired dimensions. By thus *fagoting* or *piling* the bars, their texture is rendered far more uniform, and they are made to assume a fibrous structure, which greatly increases their strength (*Merchant Bar*, or *No. 2 Bar*). To obtain the best, or *No. 3 Bar*, or *wire-iron*, these bars are doubled upon themselves, raised to a welding-heat, and again passed between rollers. These repeated rollings have the effect of thoroughly squeezing out the slag which is mechanically entangled among the particles of iron in the rough bars, and would produce flaws if allowed to remain in the metal. A slight improvement appears also to be effected in the chemical composition of the iron during the rolling, some of the carbon, silicon, phosphorus, and sulphur, still retained by the puddled iron, becoming oxidised, and passing away as carbonic oxide and slag.

The following table exhibits the change in chemical composition which takes place in pig-iron when puddled (without previous refining) and rolled into wire-iron :—

Effect of Puddling and Forging on Cast-Iron.

In 100 parts.	Carbon.	Silicon.	Sulphur.	Phosphorus.
Grey pig-iron . .	2.275	2.720	0.301	0.645
Puddled bar . . .	0.296	0.120	0.134	0.139
Wire-iron . . .	0.111	0.088	0.094	0.117

About 90 parts of bar-iron are obtained from 100 of refined iron by the puddling process, the difference representing the carbon which has passed off as carbonic oxide, and the silicon, sulphur, phosphorus, and iron, which have been removed in the slag or *tap-cinder*, this being essentially a mixture of ferrous and ferric silicates, varying much in composition according to the character of the iron employed for puddling, and the proportions of iron-scale and hammer-slag introduced into the furnace. Of course, also, the material of which the hearth is composed will influence the composition of the slag. The following table affords an illustration of its percentage composition :—

Tap-Cinder from Puddling Furnace.

Ferrous oxide (FeO) . .	57.67	Ferrous sulphide . .	7.07
Ferric oxide (Fe_2O_3) . .	13.53	Lime	4.70
Silica	8.32	Oxide of manganese . .	0.78
Phosphoric oxide (P_2O_5) .	7.29	Magnesia	0.26

The lime in the above cinder was probably derived from the hearth of the furnace, which is sometimes lined with that material to assist in removing the sulphur.

When grey pig-iron is puddled without undergoing the refining process, it becomes much more liquid than white pig or refined iron, and the process is sometimes described as the *pig-boiling process*, whilst refined iron undergoes *dry puddling*. In the latter, the oxygen of the air has more share in the de-carburising of the iron than it has in the former.

It will be observed that this process of puddling is attended with some important disadvantages; it involves a great expenditure of manual labour, and of a most exhausting kind; the very high temperature to which the puddler is exposed renders him liable to lung disease, and cataract is not uncommonly caused by the intense light from the glowing iron; the wear and tear of the puddling furnace is very considerable, and since it receives only ten or eleven charges of about 5 cwts. each in the course of twenty-four hours, it is necessary to work five or six puddling furnaces at once, in order to convert into bar-iron the whole of the cast-iron turned out from a single blast-furnace. These considerations have led to several attempts to improve the puddling process by employing revolving furnaces and other mechanical arrangements to supersede the heavy manual labour, and even to dispense with it altogether by forcing the air into the molten iron. The most generally known of the processes devised for this purpose is that of Bessemer, which consists in running the melted cast-iron into a huge crucible, and forcing air up through it under considerable pressure, thus combining the purifying influence of the blast of air in the refinery with the mechanical agitation effected in the puddling furnace. Bessemer's *converting vessel* (fig. 241) is a large, nearly cylindrical, crucible of wrought-iron, lined with *ganister* (chiefly silica, originally the road-scrapings around Sheffield), having thirty or more openings of about $\frac{1}{4}$th inch in diameter (A) at the bottom, through which air is blown at a pressure of 15 or 20 lbs. upon the inch. This vessel is sometimes large enough to receive 10 tons of cast-iron for a charge. The metal, having been melted in a separate furnace, is run into the converting vessel, previously heated by a little burning coke, the blast being already turned on so that the liquid iron may not run into the air tubes. The silicon and manganese burn first, producing a very high temperature, then the carbon is converted into carbonic oxide, which burns with a long flame at the mouth of the converter, and a little of the iron is burnt into oxide, which forms a slag with the silica and is carried up as a froth to the surface of the liquid iron. The blast of air, or *blow*, is continued for about twenty minutes, when the disappearance of the flame of carbonic oxide indicates the completion of the process; but the remaining purified iron is not pasty as in the puddling furnace, being retained in a perfectly liquid condition by the high temperature resulting from the combustion of the silicon and manganese, so that the metal may be run out into moulds by tilting the converting vessel, which is usually hung upon trunnions. In this way about 85 parts of bar-iron are obtained from 100 of pig-iron.

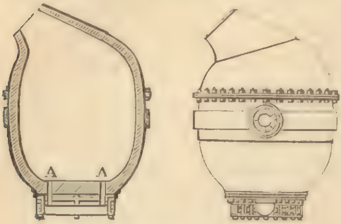

Fig. 241.—Bessemer's converting vessel.

Although so great an economy of time and labour would result from the application of Bessemer's process, it has not superseded the puddling process, because it does not remove the sulphur and phosphorus from the pig-iron, so that only the best varieties of that material, extracted from hæmatite or magnetic ore, yield a bar-iron of good quality when purified in this way. Moreover, unless the pig-iron contains much silicon or manganese, it will not produce a sufficiently high temperature in the converter, so that the original Bessemer process was applicable in this country only to the more expensive grey pig-iron, which contained much silicon and little sulphur or phosphorus, whereas the cheaper light forge-irons are best suited for puddling.

The important discovery has been made that the non-removal of the phosphorus is due to the predominance of silica, derived from the ganister lining, in the slag formed in the process, for unless there is enough base present to completely saturate the silica, the oxide of iron will combine with the silica instead of converting the phosphorus into ferrous phosphate, and carrying it off in the slag. By lining the converter with *basic bricks* made by calcining a mixture of magnesian limestone and ferric oxide, the removal of the phosphorus has been effected in the Bessemer process, and good iron has been made from cheap pig-iron containing phosphorus. (See *Bessemer steel.*) The effect of the original Bessemer process upon a particular specimen of pig-iron is shown in the following table:—

In 100 parts of Pig-iron.	Before.	After.
Carbon	3.309	0 218
Silicon	0.595	none
Sulphur	0.485	0.402
Phosphorus	1.012	1.102

In *Dankes' rotating puddling furnace* the pig-iron is run into a cylindrical chamber lined with a mixture of hæmatite and lime. Air is supplied by a fan, and the cylinder is revolved so as to bring the metal thoroughly into contact with the oxides of iron which form part of the charge, as in the ordinary puddling process. The charge of about 600 lbs. is turned out in a single ball, which is further treated as usual. In *Crampton's furnace* a very high temperature is produced by a blast of air containing coal-dust in suspension.

Composition of bar-iron.—Even the best bar-iron contains from 0.1 to 0.2 per cent. of carbon, together with minute proportions of silicon, sulphur, and phosphorus. Perfectly pure iron is inferior in hardness and tenacity to that which contains a small proportion of carbon.

Bar-iron is liable to two important defects, which are technically known as *cold-shortness* and *red-shortness.* Cold-short iron is brittle at ordinary temperatures, and appears to owe this to the presence of phosphorus, of which element 0.5 per cent. is sufficient materially to diminish the tenacity of the iron. When the iron is liable to brittleness at a red heat, it is termed red-short iron, and a very little sulphur is sufficient to affect the quality of the iron in this respect.

There is much difference of opinion as to the true causes of the variation in the strength of wrought-iron, and this is not surprising when we reflect upon the number of circumstances which may be reasonably expected to exert some influence upon it. Not only the proportions of carbon, silicon, sulphur, phosphorus, and manganese may be supposed to affect the quality of the iron, but the state of combination in which these elements exist in the mass is not unlikely to cause a difference. It also appears certain that the mechanical structure, dependent upon the arrangement of the particles composing the mass of metal, has at least as much influence upon the tenacity of the iron as its chemical composition.

The best bar-iron, if broken slowly, always exhibits a fibrous structure, the particles of iron being arranged in parallel lines. This appears to contribute greatly to the strength of the iron, for when it is wanting, and the bar is composed of a confused mass of crystals, it is weaker in proportion to the size of the crystals. The presence of phosphorus is said to favour the formation of large crystals, and hence to produce cold-shortness. There is some reason to believe that the fibrous is sometimes exchanged for the crystalline texture under the influence of frequent vibrations, as in the case of railway axles, girders of suspension-bridges, &c.

Considering the difficult fusibility of bar-iron, it is fortunate that it possesses the property of being *welded*, that is, of being united by hammering when softened by heat. It is customary first to sprinkle the heated bars with sand or clay in order to convert the superficial oxide of iron into a liquid silicate, which will be forced out from between them by hammering or rolling, leaving the clean metallic surfaces to adhere.

Manufacture of Steel.

220. Steel differs from bar-iron in possessing the property of becoming much harder when heated to redness, and then suddenly cooled by being plunged into water. Perfectly pure iron obtained by the electrotype process is not hardened by sudden cooling; but all bar-iron which contains carbon does exhibit this property in a greater or less degree according to the proportion of carbon present. It does not become decidedly steely, however, until the carbon amounts to 0.15 per cent. The term steel was formerly applied only to iron containing enough carbon (not less than 0.75 per cent.) to harden it sufficiently for cutting implements, but all iron containing more than 0.2 per cent. of carbon is now referred to as (*mild*) steel. The hardest steel contains about 1.2 per cent. of carbon, and when the proportion reaches 1.5 per cent. it begins to assume the properties of white cast-iron. Bar-iron may, therefore, be converted into *hard steel* by the addition of about 1 per cent. of carbon, and, conversely, cast-iron is converted into *mild steel* when the quantity of carbon contained in it is reduced to 0.2 to 0.5 per cent.*

Hard steel is made by the process of *cementation*, the bars of iron being imbedded in charcoal and exposed for several days to a high temperature.

The operation is effected in large chests of firebrick or stone, about 10 or 12 feet long by 3 feet wide and 3 feet deep.

Two of these chests are built into a dome-shaped furnace (*converting furnace*, fig. 242), so that the flame may circulate round them, and the furnace is surrounded with a conical jacket of brickwork in order to allow a steady temperature to be maintained in it for some days. The charcoal is ground so as to pass through a sieve of $\frac{1}{4}$-inch mesh, and spread in an even layer upon the bottom of the chests. Upon this the

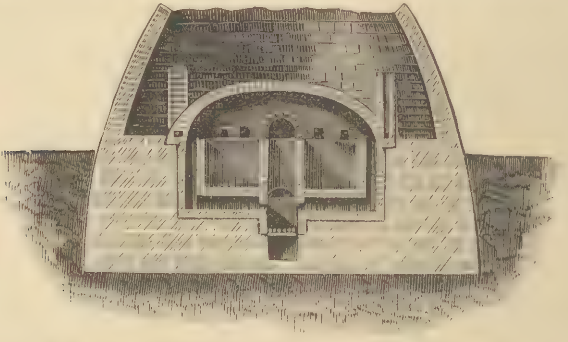

Fig. 242.—Furnace for converting bar-iron into steel.

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* Many metallurgists are of opinion that manganese has an influence similar to that of carbon in converting iron into steel.

bars of iron, which must be of the best quality, are laid in regular order, a small interval being left between them, which is afterwards filled in with the charcoal powder, with a layer of which the bars are now covered; over this more bars are laid, then another layer of charcoal, and so on until the chest is filled. Each chest holds 5 or 6 tons of bars. One of the bars is allowed to project through an opening in the end of the chest, so that the workmen may withdraw it from time to time and judge of the progress of the operation. The whole is covered in with a layer of about 6 inches of damp clay or sand, or *grinder's waste* (silica and oxide of iron).

The fire is carefully and gradually lighted, lest the chests should be split by too sudden application of heat, and the temperature is eventually raised to about the fusing point of copper (2000° F.), at which it is maintained for a period varying with the quality of steel which it is desired to obtain. Six or eight days suffice to produce steel of moderate hardness; but the process is continued for three or four days longer if very hard steel be required. The fire is gradually extinguished, so that the chests are about ten days in cooling down.

On opening the chests the bars are found to have suffered a remarkable change both in their external appearance and internal structure. They are covered with large blisters, obviously produced by some gaseous substance raising the softened surface of the metal in its attempt to escape. It is conjectured that the blisters are caused by carbonic oxide produced by the action of the carbon upon particles of slag accidentally present in the bar. On breaking the bars across, the fracture is found to have a finely granular structure, instead of the fibrous appearance exhibited by bar-iron. Chemical analysis shows that the iron has combined with about 1 per cent. of carbon, and the most remarkable part of the result is that this carbon is not only found in the external layer of iron, which has been in direct contact with the heated charcoal, but is also present in the very centre of the bar. It is this transmission of the solid carbon through the solid mass of iron which is implied by the term *cementation*. The chemistry of the process probably consists in the formation of carbonic oxide from the small quantity of atmospheric oxygen in the chest, and the removal of one-half of the carbon from this carbonic oxide, by the iron, which it converts into steel, leaving carbonic acid gas ($2CO - C = CO_2$) to be reconverted into carbonic oxide by taking up more carbon from the charcoal ($CO_2 + C = 2CO$), which it transfers again to the iron. Experiment has shown that soft iron is capable of absorbing mechanically 4.15 volumes of carbonic oxide at a low red heat, so that the action of the gas upon the metal may occur throughout the substance of the bar. The carbonic oxide is retained unaltered by the iron after cooling, unless the bar is raised to the temperature required for the production of steel.

The *blistered steel* obtained by this process is, as would be expected, far from uniform either in composition or in texture; some portions of the bar contain more carbon than others, and the interior contains numerous cavities. In order to improve its quality it is subjected to a process of fagoting similar to that mentioned in the case of bar-iron; the bars of blistered steel, being cut into short lengths, are made up into bundles, which are raised to a welding heat, and placed under a tilt-hammer, weighing about 2 cwt., which strikes two or three hundred blows in a minute; in this way the several bars are consolidated into one compound bar, which is then extended under the hammer till of the required dimensions. The bars, before being hammered, are sprinkled with sand, which combines with the oxide of iron upon the surface, and forms a vitreous layer which protects the bar from further oxidation. The steel which has been thus hammered is much denser and more uniform in composition; its tenacity, malleability, and ductility are greatly increased, and it is fitted for the manufacture of shears, files, and other tools. It is commonly known as *shear steel.* Double shear steel is obtained by breaking the tilted bars in two, and welding these into a compound bar.

The best variety of steel, however, which is perfectly homogeneous in composition, is that known as *cast-steel* or *crucible steel*, to obtain which about 50 lbs. of blistered steel are broken into fragments, and fused in a fireclay or plumbago crucible, heated in a wind-furnace, the surface of the metal being protected from oxidation by a little glass melted upon it. The fused steel is cast into ingots, several crucibles being emptied simultaneously into the same mould. Cast-steel is far superior in density and hardness to shear steel, but since it is exceedingly brittle at a red heat, great care is necessary in forging it. It has been found that the addition, to 100 parts of the cast-steel, of 1 part of a mixture of charcoal and oxide of manganese, produces a fine-grained steel which admits of being cast on to a bar of wrought-iron in the ingot-mould, so that the tenacity of the latter may compensate for the brittleness of the steel when the compound bar is forged, the wrought-iron forming the back of the implement, and the steel its cutting edge.

This addition of manganese to the cast-steel (Heath's patent) has effected a great reduction in its cost, allowing the use of blister steel made from British bar-iron, whereas, before its introduction, only the expensive iron of Swedish or Russian make could be employed. Manganese has a stronger attraction than iron has for oxygen and sulphur; hence it would decompose any sulphide or oxide of iron present in the metal, and carry those elements into the slag.

After the steel has been forged into the shape of any implement, it is hardened by being heated to redness, and suddenly chilled in cold water, or oil,* or mercury. It can thus be rendered nearly as hard as diamond, at the same time increasing slightly in volume (sp. gr. of cast-steel 7.93; after hardening, 7.66). The chemical difference between hard and soft steel appears to be of the same kind as that between grey and white cast-iron (page 315) the greater proportion of the carbon in hard steel being in combination with the metal, while in soft steel the greater part seems to be in intimate mechanical admixture with the iron, for it is left undissolved on treating the steel with an acid. If the hardened steel be heated to redness, and allowed to cool slowly, it is again converted into soft steel, but by heating it to a temperature short of a red heat, its hardness may be proportionally reduced. This is taken advantage of in annealing the steel or "letting it down" to the proper temper. The very hardest steel is almost as brittle as glass, and totally unfit for any ordinary use, but by heating it to a given temperature and allowing it to cool, its elasticity may be increased to the desired extent, without reducing its hardness below that required for the implement in hand. On heating a steel blade gradually over a flame, it will acquire a light yellow colour when its temperature reaches 430° F., from the formation of a thin film of oxide; as the temperature rises the thickness of the film increases, and at 470° a decided yellow colour is seen, which assumes a brown shade at 490°, becomes purple at 520°, and blue at 550.° At a still higher temperature the film of oxide becomes so thick as to be black and opaque. Steel which has been heated to 430°, and allowed to cool slowly, is said to be *tempered to the yellow*, and is hard enough to take a very fine cutting edge, whilst, if *tempered to the blue*, at 550°, it is too soft to take a very keen edge, but has a very high degree of elasticity. The following table indicates the tempering heats for various implements :—

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* Chilling in oil cools the steel less suddenly, on account of the lower specific heat of oil, and therefore does not render it so hard and brittle. It is often spoken of as *toughening*.

Tempering of Steel.

Temperature, F.	Colour.	Implements thus Tempered.
430° to 450°	Straw-yellow	Razors, lancets.
470°	Yellow	Penknives.
490°	Brown-yellow	Large shears for cutting metal.
510°	Brown-purple	Clasp-knives.
520°	Purple	Table-knives.
530° to 570°	Blue	Watch-springs, sword-blades.

If a knife blade be heated to redness its *temper is spoilt*, for it is converted into soft steel.

In general, the steel implements are ground after being tempered, so that they are not seen of the colours mentioned above, except in the case of watch-springs.

A steel blade may be easily distinguished from iron by placing a drop of diluted nitric acid upon it, when a dark stain is produced upon the steel, from the separation of the carbon.

Some small instruments, such as keys, gun-locks, &c., which are exposed to considerable wear and tear by friction, and require the external hardness of steel without its brittleness, are forged from bar-iron, and converted externally into steel by the process of *case-hardening*, which consists in heating them in contact with some substance containing carbon (such as bone-dust, yellow prussiate of potash, &c.), and afterwards chilling in water. A process which is the reverse of this is adopted in order to increase the tenacity of stirrups, bits, and similar articles made of cast-iron; by heating them for some hours in contact with oxide of iron or manganese, their carbon and silicon are removed in the forms of carbonic oxide and silica, and they become converted into *malleable cast-iron*.

A similar effect is produced by heating in sand, the air between its grains affording the required oxygen.

The opinion that steel owes its properties entirely to the presence of carbon is not universally entertained. Some chemists believe that nitrogen (or some analogous element) is an indispensable constituent, but the proportion of nitrogen found in steel is too minute to warrant this supposition. Titanium is alleged by some authorities to have an important influence upon the quality of steel, but this also appears to be a doubtful matter. Bar-iron may be converted into steel by being kept at a high temperature in an atmosphere of coal gas, from which it abstracts carbon.

Bessemer steel was originally produced by arresting the purification of cast-iron in Bessemer's process (page 322), as soon as the carbon had diminished to the required proportion, when the steel was poured out in the fused state, *i.e.*, in the form of cast-steel; and this is still occasionally done when a pig-iron containing about 3 per cent. of manganese can be obtained, the blow being stopped when the carbon has been diminished to 0.3 or 0.4 per cent., and the manganese to 0.2 per cent. A steel of better quality, however, has been obtained by continuing the purification until liquid bar-iron remains in the converter, and introducing the proper proportion of carbon in the form of a peculiar description of white cast-iron known as *Spiegel-eisen* (mirror-iron), which crystallises in lustrous tabular crystals, and contains large proportions of carbon and manganese, being obtained by smelting spathic iron ore rich in manganese, with charcoal as fuel. The *Spiegel-eisen* is added, in a melted state, to the Bessemer iron before pouring from the converter.

The composition of a sample of *Spiegel-eisen* smelted from a spathic ore, found near Müsen in Prussia, is here given :—

Iron	82.86	Silicon	1.00
Manganese	10.71	Carbon	4.32

Ferro-manganese, which is also employed in the manufacture of steel, is extracted from certain manganese ores, and contains iron with about 74 per cent. of manganese, 5 per cent. of carbon, and 1 per cent. of silicon. Since the pig-iron obtained from clay ironstones is not well adapted for conversion into Bessemer steel, large quantities of hæmatite are imported for this manufacture from Bilbao (Spain), Elba, Algeria, &c.

Bessemer steel is now made very cheaply from the inferior pig-iron containing phosphorus by the *Thomas-Gilchrist* or *basic process*, in which the difficulty in removing phosphorus has been overcome by lining the converter with calcined magnesian limestone (mixed with tar) so as to secure a basic slag which could not be obtained when the converter was lined with siliceous ganister (see p. 322).

Siemens-Martin steel is made by melting together, in a Siemens regenerative furnace, pig-iron rich in manganese, and puddled iron, together with steel-scrap and ferro-manganese, some magnetic iron ore being also sometimes added as an oxidising agent to diminish the carbon. Samples of this steel were found to contain, in 100 parts—

	Hard.	Medium.	Soft.
Carbon	0.67	0.35	0.16
Manganese	0.40	0.18	0.14

The soft variety was prepared for boiler-plates.

Puddled steel is obtained by arresting the puddling process at an earlier stage than usual, so as to leave a proportion of carbon varying from 0.3 to 1 per cent. It is necessary that manganese should be present, in order to render the slag sufficiently fluid at the lower temperature at which the *balling* is effected when the more fusible steel is produced.

Natural steel or *German steel* results in a similar way, from the incomplete purification of cast-iron in the refinery. The presence of manganese in the iron is favourable to its production.

Krupp's cast-steel, manufactured at Essen near Cologne, and employed for ordnance, shells, &c., is a puddled steel made from hæmatite and spathic ore, smelted with coke. The iron thus obtained contains much manganese, which is removed in the puddling process. Krupp's steel contains about 1.2 per cent. of combined carbon, and is fused with a little bar-iron for casting ordnance. The fusion is effected in black lead crucibles holding 30 lbs. each, of which as many as 1200 are emptied simultaneously into the mould for the largest castings. A casting of 16 tons requires about 400 men, who act together in well-disciplined gangs, so that the stream of molten metal shall flow continuously along the gutters into the mould. Such large castings must be allowed to cool very gradually, so that they are kept surrounded with hot cinders, sometimes for two or three months, till required for forging.

Siemens' process for producing steel directly from the ore consists in mixing it with fluxing and reducing materials, and heating it in a rotating furnace lined with Bauxite bricks (p. 301), and supplied with heated air from a regenerator (313). A spongy mass of metal is thus obtained, like that from the puddling furnace, but richer in carbon. This is afterwards fused with a little cast-iron to obtain a mild steel containing less than 0.24 per cent. of carbon.

The soundness of steel ingots is often impaired by minute bubbles or *blowholes* formed by carbonic oxide or hydrogen, the former produced by the action of the carburised iron upon a portion of oxidised iron, the latter by the decomposition of moisture in the air. To obviate this, the steel is sometimes subjected to a pressure of several tons on the square inch while it is solidifying (*Whitworth steel*).

221. *Direct extraction of wrought-iron from the ore.*—Where very rich and pure ores of iron, such as hæmatite and magnetic iron ore, are obtainable, and fuel is abundant, the metal is sometimes extracted without being converted into cast-iron. It is probable that the iron of antiquity was extracted in this way, for it is doubtful whether cast-iron was known to the ancients, and the slag left from old iron-works does not indicate the use of any flux. Some works of this description are still in operation in the Pyrenees, where the *Catalan process* (fig. 243) is employed. The crucible is lined at the sides with thick iron plates, and at the bottom with a refractory stone. A quantity of red-hot charcoal is thrown into it, and the space above this is temporarily divided into two compartments by a shovel. The compartment nearest to the pipe through which the blast enters is charged with charcoal, and the other compartment with the calcined ore in small pieces. The shovel is then withdrawn, and a gradually increasing current of air supplied, fresh ore and fuel being added as they sink down. One part of the oxide of iron is reduced to the metallic state by the carbonic oxide, and the rest combines with the silica present in the ore to form a slag. After about five hours the spongy masses of bar-iron are collected into a ball upon the end of an iron rod, and hammered into a compact mass like the metal obtained in the puddling furnace. The blowing machine employed in the Pyrenees is one in which the fall of water from a cistern down a long wooden pipe, sucks in, through lateral apertures, a supply of air which it carries down with it into a box, from which the pressure of the column of water projects it with some force through the blast-pipe, the water escaping from the box through another aperture.

In the North American *bloomery forges* a modernised form of the same process is adopted.

The wrought-iron produced by this process always contains a larger proportion of carbon than puddled iron, and is therefore somewhat steely in character. In India the native smelters produce iron or steel at will by this process. The blast furnace (p. 311) is really a development of the Catalan forge, the hearth being enclosed so that the temperature is raised and the iron more highly carburised.

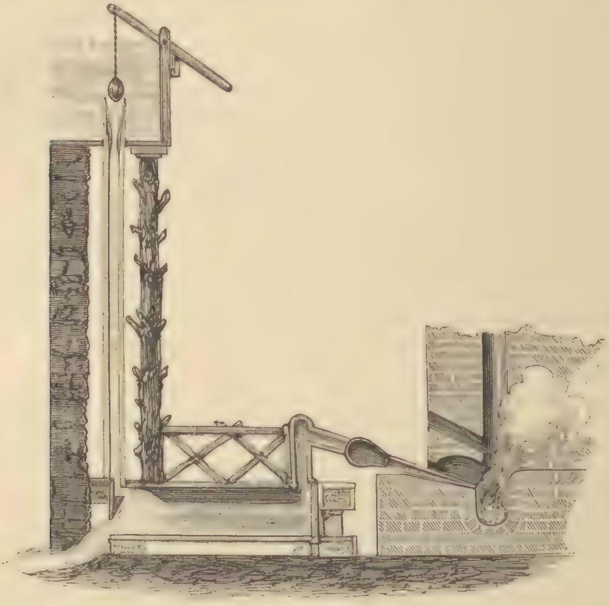

Fig. 243.—Catalan forge for smelting iron ores.

222. *Extraction of iron on the small scale.*—In the laboratory, iron may be extracted from hæmatite in the following manner:—A fireclay crucible (A, fig. 244), about 3 inches high, is filled with charcoal powder, rammed down in successive layers; a smooth conical cavity is scooped in the charcoal, and a mixture of 100 grs. red hæmatite, 25 grs. chalk, and 25 grs. pipe-clay is introduced into it; the mixture is covered with a layer of charcoal, and a lid placed on the crucible, which is heated in a Sefström blast-furnace,* fed with coke in small pieces, for about half an hour. On breaking the cold crucible a button of cast-iron will be obtained.

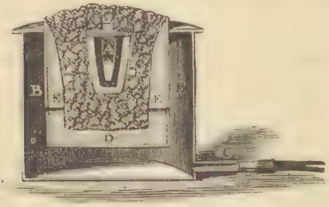

Fig. 244.— Sefström furnace.

Nearly pure iron may be prepared by fusing the best wire-iron with about one-fifth of its weight of pure ferric oxide, to oxidise the carbon and silicon which it contains. Some powdered green glass, perfectly free from lead, must be employed as a flux, and the crucible (with its cover well cemented on with fireclay) exposed for an hour to a very high temperature. A silvery button of iron will then be obtained.

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* This very useful furnace, shown in section in fig. 244, consists of two iron cylinders with a space (B) between them, into which air is forced through the tube C by a double-action bellows. The inner cylinder has a fireclay lining (D), through which four or six copper tubes (E) admit the blast into the fuel.

223. *Chemical properties of iron.*—In its ordinary condition iron is unaffected by perfectly dry air, but in the presence of moisture and carbonic acid gas it is gradually converted into hydrated ferric oxide ($2Fe_2O_3.3H_2O$) or *rust*. The water is decomposed, and ferrous carbonate formed ($Fe + H_2O + CO_2 = FeCO_3 + H_2$); this is dissolved by the carbonic acid present, and the solution rapidly absorbs oxygen from the air, depositing the ferric oxide in a hydrated state; $2FeCO_3 + O = Fe_2O_3 + 2CO_2$. When iron nails are driven into a new oaken fence, a black streak will soon be observed descending from each nail, caused by the formation of tannate of iron (ink) by the action of the tannic acid in the wood upon the solution of carbonate of iron formed from the nails. The diffusion of *iron-mould* stains through the fibre of wet linen by contact with a nail, is also caused by the formation of solution of carbonate of iron. The iron in *chalybeate* waters is also generally present in the form of carbonate dissolved in carbonic acid, and hence the rusty deposit which is formed when they are exposed to the air. Iron does not rust in water containing a free alkali, or alkaline earth, or an alkaline carbonate.

Concentrated sulphuric and nitric acids do not act upon iron at the ordinary temperature, though they dissolve it rapidly when diluted. Even when boiling, strong sulphuric acid acts upon it but slowly. When iron has been immersed in strong nitric acid (sp. gr. 1.45), it is found to be unacted upon when subsequently placed in nitric acid of sp. gr. 1.35, unless previously wiped; it is then said to have assumed the *passive state.* If iron wire be placed in nitric acid of sp. gr. 1.35, it is acted upon immediately, but if a piece of gold or platinum be made to touch it beneath the acid, the iron assumes the passive state, and the action ceases at once. A state similar to this, the cause of which has not yet been satisfactorily explained, is sometimes assumed by the other metals, though in a less marked degree. In the case of iron it has been attributed to the formation of a coating of the magnetic oxide, which is sparingly soluble in strong nitric acid.

Ferrum redactum is iron in powder obtained by reducing ferric oxide with hydrogen at a red heat in an iron tube. It always contains some Fe_3O_4.

224. *Oxides of iron.*—Three compounds of iron with oxygen are known in the separate state—FeO, Fe_3O_4, Fe_2O_3.

Ferrous oxide, or *protoxide of iron*, FeO, is obtained by heating ferric oxide to 500° C. in dry hydrogen; $Fe_2O_3 + H_2 = H_2O + 2FeO$. It is obtained as a grey powder, which readily absorbs O from the air, taking fire and becoming Fe_3O_4. It is a basic oxide, yielding ferrous salts. In the finely divided state it decomposes water.

Ferrous hydrate, $Fe(HO)_2$, is precipitated by alkalies from the ferrous salts. When pure it forms a white precipitate, but if air be present it becomes green from the production of ferroso-ferric oxide, and ultimately brown ferric hydrate. These changes are best seen when potash or ammonia is added to the ferrous salt obtained by shaking iron turnings or filings with a strong solution of sulphurous acid. This disposition of the ferrous hydrate to absorb oxygen is turned to advantage when a mixture of ferrous sulphate with lime or potash is employed for converting blue into white indigo. The ferrous oxide is a strong base.

Ferric oxide, or *peroxide of iron*, Fe_2O_3, occurs as *specular iron ore* in six-sided crystals, and in hæmatite, as already noticed among the ores of iron, and has also been referred to as occurring in commerce under the names of *colcothar*, *jeweller's rouge*, and *Venetian red*, which are obtained by the calcination of the green sulphate of iron; $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. The hydrate, obtained by decomposing a solution of ferric chloride with an alkali, forms a brown gelatinous precipitate, which is easily dissolved by acids. When dried at 100° C., it becomes $2Fe_2O_3.H_2O$. If a hot solution of a ferric salt be precipitated by an alkali, and the precipitate dried over sulphuric acid, it becomes $Fe_2(HO)_6.Fe_2O_3$, which is the composition of iron-rust and of some brown hæmatites. When either of the hydrates is heated to dull redness, it exhibits a sudden glow, and is converted into a modification of Fe_2O_3, which is dissolved with great difficulty by acids, although it has the same composition as the soluble form which has not been strongly heated. When the ferric oxide is heated to whiteness, it loses oxygen, and is converted into magnetic oxide of iron; $3Fe_2O_3 = 2Fe_3O_4 + O$. Existing as it does in all soils, ferric oxide is believed to fulfil the purpose of oxidising the organic matter in the soil, and converting its carbon into carbon dioxide, to be absorbed by the plant; the ferric oxide being thus reduced to ferrous oxide, which is oxidised by the air, and fitted to perform again the same office. Ferric oxide, like alumina, is a weak base, and even exhibits some tendency to play the part of an acid towards strong bases, though not in so marked a degree as alumina. When Fe_2O_3 is heated in a stream of H or CO, it yields Fe_3O_4 at 350° C., pyrophoric FeO at 500° C., and metallic iron at from 700° to 800° C.

Magnetic or *black oxide of iron*, or *magnetite*, Fe_3O_4, is generally regarded as a compound of ferrous oxide with ferric oxide ($FeO.Fe_2O_3$), a view which is confirmed by the occurrence of a number of minerals having the same crystalline form as the native magnetic oxide of iron, in which the iron, or part of it, is displaced by other metals. Thus, *spinelle* is $MgO.Al_2O_3$; *Franklinite*, $ZnO.Fe_2O_3$; chrome-iron ore, $FeO.Cr_2O_3$; *pleonaste*, $MgO.Fe_2O_3$; *Gahnite*, $ZnO.Al_2O_3$. The natural magnetic oxide was mentioned among the ores of iron, and this oxide has been seen to be the result of the action of air or steam upon iron at a high temperature. The hydrated magnetic oxide of iron ($Fe_3O_4.H_2O$) is obtained as a black crystalline powder by mixing 1 molecule of ferrous sulphate with 1 molecule of ferric sulphate, and pouring the mixture into a slight excess of solution of ammonia, which is afterwards boiled with it. Magnetic oxide of iron, when acted upon by acids, yields mixtures of ferrous and ferric salts, so that it is not an independent basic oxide.

The very stable character of Fe_3O_4 has led to its application for protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense strongly adherent film of Fe_3O_4 is produced, which effectually protects the metal (*Barff's process*). A similar coating is produced by the action of a mixture of air and carbonic acid gas (*Bower's process*).

Ferric acid, H_2FeO_4, has not been obtained in the free state.

When iron filings are strongly heated with nitre, and the mass treated with a little water, a fine purple solution of potassium ferrate is obtained. A better method of preparing this salt consists in suspending 1 part of freshly precipitated ferric hydrate in 50 parts of water, adding 30 parts of solid potassium hydrate, and passing chlorine till a slight effervescence commences; $Fe_2O_3 + Cl_6 + 10KHO = 6KCl + 2(K_2FeO_4) + 5H_2O$; the ferrate forms a black precipitate, being insoluble in the strongly alkaline solution, though it dissolves in pure water to form a purple solution, which is decomposed even by dilution, oxygen escaping, and hydrated ferric oxide being precipitated. A similar decomposition takes place on boiling a strong solution, or on adding an acid with a view to liberate the ferric acid. The ferrates of barium, strontium, and calcium are obtained as fine red precipitates when solutions of their salts are mixed with potassium ferrate.

As a lecture experiment, the ferrate is readily prepared by dissolving a fragment of KHO in a little solution of Fe_2Cl_6, adding a few drops of bromine, and gently heating. On dissolving the cold mass in water, a fine red solution is obtained, which gives a red granular precipitate with $BaCl_2$.

The pink solution obtained by boiling some samples of chloride of lime with water contains calcium ferrate, and gives a pink precipitate with $BaCl_2$. By boiling Fe_2Cl_6 with excess of chloride of lime, a fine pink solution of calcium ferrate is obtained.

Ferrous carbonate, $FeCO_3$, or *spathic iron ore*, or *siderite*, is found in rhombohedral crystals associated with the carbonates of Ca, Mg, and Mn, which are isomorphous with it. It occurs in chalybeate waters, dissolved in carbonic acid, and deposits as ferric hydrate when the water is exposed to air.

If powdered iron which has been reduced from the oxide by hydrogen (*ferrum redactum*) be suspended in water, and a stream of CO_2 be passed for some time, a solution of ferrous carbonate in carbonic acid is obtained, which, when filtered, is colourless, becomes rusty when exposed to air, and gives, when boiled, an abundant precipitate of $FeCO_3$, which is nearly white, and becomes green when exposed to air.

Sodium carbonate added to a ferrous salt gives a white precipitate if all air be excluded; otherwise, oxygen is absorbed and a dingy green precipitate containing Fe_3O_4 is formed.

The substance sold as *ferric carbonate*, obtained by precipitating a ferric salt with sodium carbonate, is mainly ferric hydrate, since weak bases like Fe_2O_3 do not form carbonates.

225. *Ferrous sulphate*, *copperas*, *green vitriol*, or *sulphate of iron*, is easily obtained by heating 1 part of iron wire with 1½ part of strong sulphuric acid, mixed with 4 times its weight of water, until the whole of the metal is dissolved, when the solution is allowed to crystallise. Its manufacture on the large scale by the oxidation of iron pyrites has been already referred to. It forms fine green rhomboidal crystals, having the composition $FeSO_4.H_2O.6Aq$.

The colour of the crystals varies somewhat, from the occasional presence of small quantities of ferric sulphate, $Fe_2(SO_4)_3$. It dissolves very easily in twice its weight of cold water, yielding a pale green solution. One part of boiling water dissolves about 2.5 parts of the crystals. When the commercial sulphate of iron is boiled with water, it yields a brown muddy solution, in consequence of the decomposition of the ferric sulphate contained in it, with precipitation of a basic sulphate. Ferrous sulphate has a great tendency to absorb oxygen, and to become converted into ferric sulphate. Thus, the ordinary crystals when exposed to air gradually become brown, and are converted into a mixture of the normal and basic ferric sulphates.

This disposition to absorb oxygen renders the ferrous sulphate useful as a reducing agent; thus, it is employed for precipitating gold in the metallic state from its solutions. But its chief use is for the manufacture of ink and black dyes by its action upon vegetable infusions containing tannic acid, such as that of nut-galls. This application will be more particularly noticed hereafter.

Crystals of $FeSO_4.H_2O.4Aq$, isomorphous with $CuSO_4.H_2O.4Aq$, may be obtained by dropping a crystal of cupric sulphate into a supersaturated solution of ferrous sulphate.

The salt $FeSO_4.SO_3$ is obtained in minute prismatic crystals when a saturated solution of ferrous sulphate is added to an excess of strong sulphuric acid.

Ferric sulphate, $Fe_2(SO_4)_3$, is found in Chili as a white silky crystalline mineral, *coquimbite*, having the composition $Fe_2(SO_4)_3.9Aq$.

Ferrous phosphate, $Fe_3(PO_4)_2$, and *arsenate*, $Fe_3(AsO_4)_2$, are used in medicine, being prepared by precipitating ferrous sulphate with a mixture of sodium acetate and sodium phosphate or arsenate. The acetate is used so that the resulting liquid may contain free acetic acid instead of the free sulphuric formed by the H in the sodium salt; $3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + Na_2SO_4 + H_2SO_4$. Both the phosphate and arsenate are white when perfectly pure, but they become blue when exposed to air, from the production of a little ferroso-ferric salt. The precipitated *ferric phosphate* is $2FePO_4.5Aq$. Ferrous phosphate is found in the mineral *Vivianite*, or *native Prussian blue*, $Fe_3(PO_4)_2.8Aq$.

Ferrous silicate, Fe_2SiO_4, is found crystallised in *finery cinder* of the iron-works.

Ferrous chloride, $FeCl_2$, sublimes in colourless six-sided scales when iron is heated in HCl gas. It is deliquescent, and crystallises from water in pale green crystals, $FeCl_2.4Aq$, which are oxidised by air.

Ferrous iodide, FeI_2, is prepared by digesting fine iron wire with twice its weight of iodine and about eight parts of water for some time, afterwards boiling till the red colour has disappeared, filtering, and evaporating down in contact with clean iron. It forms green crystals, $FeI_2.4Aq$, which are deliquescent and very soluble in water. The solution absorbs oxygen from the air, and deposits a brown precipitate unless kept in contact with clean iron or mixed with strong syrup.

226. *Ferric chloride*, or *perchloride of iron* (Fe_2Cl_6), is obtained in beautiful dark green crystalline scales when iron wire is heated in a glass tube through which a current of dry chlorine is passed, the ferric chloride passing off in vapour, and condensing in the cool part of the tube. The crystals almost instantly become wet when exposed to air on account of their great attraction for water. Ferric chloride may be obtained in solution by dissolving iron in hydrochloric acid, and converting the ferrous chloride ($FeCl_2$) thus formed into ferric chloride by the action of nitric and hydrochloric acids (p. 170). A strong solution yields crystals of $Fe_2Cl_6.2Aq$. The aqueous solution reddens litmus. The crystals are decomposed by heat, leaving an oxychloride. The solution of ferric chloride has been recommended in some cases as a disinfectant, being easily reduced to ferrous chloride, and thus affording chlorine to unstable organic matters (p. 154). In contact with paper, Fe_2Cl_6 becomes reduced to $FeCl_2$ when exposed to light. A solution of perchloride of iron in alcohol is used in medicine under the name of *tincture of iron*. It is also soluble in ether.

Solution of ferric chloride is capable of dissolving a very large quantity of *pure* freshly precipitated ferric oxide, nine molecules of Fe_2O_3 being dissolved by one molecule of Fe_2Cl_6. The solution of ferric *oxychloride* thus obtained has a very dark red colour, and yields a very copious brown precipitate with common water, or any solution containing even a trace of a sulphate. By dialysis, an aqueous solution of ferric oxide is left in the dialyser.

Ferrous sulphide, FeS, is formed when a red-hot bar of iron is rubbed with a stick of sulphur, the fused FeS running off in globules. It is usually prepared by mixing 3 parts of iron filings with 2 parts of sulphur, and throwing the mixture, a little at a time, into a red-hot crucible, when it forms a fused metallic-looking mass. It is obtained as a black precipitate when an alkaline sulphide is added to a ferrous salt. It is easily oxidised when exposed to air in a moist state, and dissolves readily in HCl, being indeed the only black sulphide which dissolves easily in dilute HCl. It is used in the laboratory for making H_2S.

Magnetic pyrites, Fe_7S_8, is found in yellow six-sided crystals.

Iron pyrites, or *mundic*, FeS_2, forms yellow cubes or octahedra of sp. gr. 5.2. It is formed by the slow reduction of ferrous sulphate by organic matter, and its presence in coal appears to be accounted for in this way. Minute crystals of iron pyrites are sometimes found as rough casts of organic substances. It burns when heated, yielding Fe_2O_3 and SO_2, and is largely used as a source of the latter by the vitriol manufacturer. Sulphur itself may be obtained from it by distillation at a high temperature, Fe_3S_4 being left. FeS_2 is insoluble in HCl, which distinguishes it from FeS. It may be dissolved by nitric acid. *Radiated pyrites*, or white pyrites, or *marcasite*, has the same composition, but its sp. gr. is only 4.8.

Some kinds of pyrites explode with considerable violence when heated, and create much alarm when they occur in household coal; these have been found to contain small cavities filled with highly compressed (probably liquid) CO_2, which expands suddenly when heated.

Compact yellow iron pyrites is not oxidised by exposure to air, but white pyrites is easily converted into ferrous sulphate and sulphuric acid, the oxidation being attended by so much heat as to set fire to coal. Even yellow pyrites in minute crystals diffused through clay will behave in the same way.

The FeS_2 may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydrate moderately in a stream of H_2S as long as it increases in weight.

Ferrous silicide, Fe_2Si, has been obtained by fusing red hæmatite with sand and charcoal. It is insoluble in hydrochloric acid and dissolves but slightly in aqua regia, even after long boiling.

Iron nitride, a compound of iron with about 9 per cent. of nitrogen, has been found as a silvery deposit on the lavas of Etna. It yields ammonia when heated in hydrogen.

227. *Atomic weight of iron.*—When iron is dissolved in hydrochloric acid, 28 parts by weight of iron combine with 35.5 parts of chlorine, displacing 1 part of hydrogen. The specific heat of iron, and its isomorphism with magnesium, zinc, and cadmium, show that its atomic weight must be represented by 56, so that iron is a diad or divalent element, one atom of iron being exchangeable for two atoms of hydrogen.

The molecular formula of ferric chloride has been confirmed by the determination of the specific gravity of its vapour, which has been found to be 165 times that of hydrogen. If, therefore, one volume (or one atom) of hydrogen be represented as having a weight = 1, *two* volumes (or one molecule) of ferric chloride vapour would weigh (165×2) 330, a number nearly agreeing with the sum of two atoms of iron (112) and six atoms of chlorine (213).

It will be remarked that iron possesses a different valency accordingly as it exists in ferrous or ferric compounds. Thus, in ferrous oxide (FeO) and ferrous chloride ($FeCl_2$) it occupies the place of two atoms of hydrogen, and is diatomic; but in ferric oxide (Fe_2O_3) and ferric chloride (Fe_2Cl_6) each atom of iron occupies the place of three atoms of hydrogen, and is triatomic.

Iron is remarkable for its two series of fairly stable salts, the ferrous and ferric, the former acting as reducing agents, and the latter as oxidising agents. Ferrous iron resembles magnesium and zinc in its disposition to form double salts with salts of ammonium, hence its solutions are imperfectly precipitated by ammonia; but ferric iron resembles aluminium, and is completely precipitated. Nitric acid, chloric acid, and chlorine will always convert ferrous into ferric salts, and ensure complete precipitation by ammonia.

Some chemists designate the diatomic iron existing in ferrous compounds by the name *ferrosum* (Fe''), and the triatomic iron of the ferric compounds by *ferricum* (Fe'''). Others regard iron as a tetratomic metal Fe^{iv}, existing in the ferrous salts as a group of two atoms united by two bonds, and in the ferric salts as a group of two atoms united by one bond. On this view, ferrous chloride would be Fe_2Cl_4, or $Cl_2{=}Fe{=}Fe{=}Cl_2$, and ferric chloride would be Fe_2Cl_6, or $Cl_3{\equiv}Fe{-}Fe{\equiv}Cl_3$.

COBALT.

$Co'' = 59$ parts by weight.

228. Some of the compounds of cobalt are of considerable importance in the arts, on account of their brilliant and permanent colours. It is generally found in combination with arsenic and sulphur, forming *tin-white cobalt*, $CoAs_2$, and *cobalt glance*, $CoAs_2.CoS_2$, but its ores also generally contain nickel, copper, iron, manganese, and bismuth.

The metal itself is obtained by strongly heating the cobalt oxalate (CoC_2O_4) in a covered porcelain crucible. In its properties it closely resembles iron, but it is said to surpass it in tenacity. It is heavier than iron, sp. gr. 8.6, and rather more easily fusible.

Two *oxides of cobalt* are known—the *protoxide*, or *cobaltous oxide*, CoO, which is decidedly basic, and the *sesquioxide*, or *cobaltic oxide*, Co_2O_3, which is a very feeble base. The protoxide of cobalt, like those of iron and manganese, tends to absorb oxygen from the air, and when heated in the air, becomes converted into $CoO.Co_2O_3$, corresponding to the magnetic oxide of iron. The commercial oxide of cobalt, which is employed for painting on porcelain, is obtained by roasting the ore, in order to expel part of the sulphur and arsenic, dissolving it in hydrochloric acid, and precipitating the ferric oxide by the careful addition of lime, when the remaining arsenic is also precipitated as ferric arsenate. Hydrosulphuric acid is passed through the acid solution to precipitate the bismuth and copper, leaving the cobalt and nickel in solution. The latter, having been boiled to expel the excess of hydrosulphuric acid, is neutralised with lime and mixed with solution of chloride of lime, which precipitates the sesquioxide of cobalt as a black powder, leaving the oxide of nickel in solution, from which it may be precipitated by the addition of lime.

Cobaltous hydrate, $Co(HO)_2$, is obtained by adding potash in excess to a solution of cobaltous salt, and boiling. The blue precipitate produced at first is a basic salt which becomes converted into the red hydrate on boiling with excess of potash. If air be allowed access, it oxidises the red precipitate, converting it into brown cobaltic hydrate. Cobaltous hydrate dissolves in ammonia, giving a fine red solution which absorbs oxygen from the air and becomes brown.

Cobaltic oxide, Co_2O_3, is left as a black powder when cobaltic nitrate is gently heated. It dissolves in cold HCl, yielding a brown solution of *cobaltic chloride*, Co_2Cl_6, which is easily decomposed when heated, evolving Cl_2 and leaving $2CoCl_2$.

Cobaltic hydrate, $Co_2(HO)_6$, forms the black precipitate when the solution of a hypochlorite or hypobromite is added to a cobaltous salt.

Cobaltous nitrate, $Co(NO_3)_2.6Aq$, obtained by dissolving CoO in HNO_3 and crystallising, forms red prisms which become blue when their water is expelled, and afterwards black Co_2O_3.

Cobalt-yellow, or *potassium-cobaltic nitrite*, $K_6Co'''_2(NO_2)_{12}$, is obtained as a yellow precipitate when cobaltous nitrate is acidulated with acetic acid, and potassium nitrite added; the acetic acid liberates nitrous acid, which oxidises the cobaltous salt; $2Co''(NO_3)_2 + 10KNO_2 + 4HNO_2 = K_6Co'''_2(NO_2)_{12} + 4KNO_3 + 2NO + 2H_2O$. It forms a yellow crystalline precipitate, slightly soluble in water, and not decomposed by cold HCl or HNO_3. Caustic alkalies decompose it, separating cobaltic hydrate.

Cobaltous chloride ($CoCl_2$), obtained by dissolving either of the oxides in hydrochloric acid, forms red prisms, $CoCl_2.6Aq$, which become blue $CoCl_2.2Aq$ at 120° C., and at 140° C., $CoCl_2$, which may be sublimed in dark blue scales in a current of chlorine. If strong hydrochloric acid be added to a red solution of this salt, it becomes blue; if enough water be now added to render it pink, the blue colour may be produced at pleasure by boiling, the solution first passing through a neutral tint. Chloride (*muriate*) of cobalt is employed as a *sympathetic ink*, for characters written with its pink solution are nearly invisible till they are held before the fire, when they become blue, and resume their original pink colour if exposed to the air; a little chloride of iron causes a green colour.

The *cobaltous sulphide* (CoS) is obtained as a black precipitate when an alkaline sulphide is added to a solution of a salt of cobalt. It differs from FeS by being insoluble in HCl. A *cobaltic sulphide* (Co_2S_3) is found in grey octahedra, forming *cobalt pyrites.* The *disulphide* (CoS_2) has been obtained artificially.

Cobaltous sulphate, $CoSO_4.7H_2O$, is found as *cobalt vitriol.* It forms red prisms isomorphous with ferrous sulphate. It does not become blue when dried, and bears a high temperature without decomposing.

Cobaltous arsenate, or *cobalt bloom*, $Co_3(AsO_4)_2.8Aq$, is found in pink needles.

Cobalt di-arsenide, $CoAs_2$, is found crystallised as *tin-white cobalt* and *speiss cobalt*, in which it is associated with the isomorphous arsenides of nickel and iron, so that it is written $[CoNiFe]As_2$. $CoAs_3$ is also found in nature.

The *cobaltous silicate* associated with potassium silicate forms the blue colour known as *smalt*, which is prepared by roasting the cobalt ore, so as to convert the bulk of the cobalt into oxide, leaving, however, a considerable quantity of arsenic and sulphur still in the ore. The residue is then fused in a crucible with ground quartz and carbonate of potash, when a blue glass is formed, containing cobalt silicate and potassium silicate, whilst the iron, nickel, and copper, combined with arsenic and sulphur, collect at the bottom of the crucible and form a fused mass of metallic appearance known as *speiss*, which is employed as a source of nickel. The blue glass is poured into cold water, so that it may be more easily reduced to the fine powder in which the smalt is sold. If the cobalt ore destined for smalt be over-roasted, so as to convert the iron into oxide, this will pass into the smalt as a silicate, injuring its colour. Smalt much resembles ultramarine, but is not bleached by acids.

Zaffre is prepared by roasting a mixture of cobalt ore with two or three parts of sand.

Thénard's blue, or *cobalt ultramarine*, consists of cobalt phosphate and aluminium phosphate, and is prepared by mixing precipitated alumina with cobalt phosphate and calcining in a covered crucible. The phosphate is obtained by precipitating a solution of cobalt nitrate with phosphate of potassium or sodium.

Rinmann's green is prepared by calcining the precipitate produced by sodium carbonate in a mixture of cobalt sulphate with zinc sulphate. It is a compound of the oxides of cobalt and zinc.

The *relations of ammonia to the cobalt salts* are very remarkable and characteristic, the NH_3 combining both with cobaltous and cobaltic salts to form compounds which behave like salts of new bases containing cobalt, nitrogen, and hydrogen.

When solution of NH_3 is added to $CoCl_2$, and air is excluded, the red *cobaltoso-ammonic chloride* is formed—

$$CoCl_2 + 6NH_3 = Cl(NH_3)_3Co''(NH_3)_3Cl.$$

If the solution be exposed to air, it becomes much darker, and on adding strong HCl in excess, it deposits crystals of *di-cobaltic hexammonic chloride*; $Co_2Cl_6 + 6NH_3 = Cl_3(NH_3)_3Co'''_2(NH_3)_3Cl_3$. A large number of beautifully coloured compounds of a similar nature have been prepared. They are generally referred to as *cobaltamine compounds*.

Cobalt is seen to resemble iron in many respects, but the cobaltic compounds are much less stable than the ferric compounds. Cobaltous compounds become oxidised to cobaltic compounds only in solutions which are neutral or alkaline, while ferrous compounds are easily oxidised in acid solutions. No compounds corresponding to the cobaltamine compounds are obtained with iron. But both iron and cobalt form remarkable compounds with potassium and cyanogen, iron forming the ferrocyanide, $K_4Fe''Cy_6$, and ferricyanide, $K_3Fe'''Cy_6$, while cobalt forms the cobalticyanide, $K_3Co'''Cy_6$.

NICKEL.

$Ni'' = 59$ parts by weight.

229. Nickel owes its value in the useful arts chiefly to its property of imparting a white colour to the alloys of copper and zinc, with which it forms the alloy known as *German silver*. Alloys of copper and nickel are used in coinage. Nickel is very nearly allied to cobalt, and generally occurs associated with that metal in its ores. One of the principal ores of nickel is the *Kupfernickel*, or copper-nickel, so called by the German miners because they frequently mistook it for an ore of copper; it has a reddish metallic appearance, and the formula NiAs. *Grey nickel ore*, or *nickel glance*, is an arseniosulphide of nickel, $NiAs_2.NiS_2$. *Arsenical nickel*, $NiAs_2$, corresponds to tin-white cobalt. The metal is commonly extracted from the *speiss* separated during the preparation of smalt from cobalt ores. It is now generally sent into commerce in small cubes which are made from the nickel hydrate precipitated by lime (p. 336). This is ignited, the residual NiO washed with weak

HCl to remove lime, and pressed into the shape of cubes, which are strongly heated with powdered charcoal, and thus reduced to the metallic state. They contain a little carbon, as well as other impurities.

Nickel is now extracted from an ore found in New Caledonia, which consists of silicates of nickel, iron, and magnesium, containing 24 per cent. of nickel. The ore is treated with sulphuric acid, and the solution mixed with ammonium sulphate. On evaporation, nickel ammonium sulphate is deposited in crystals, which are purified by recrystallisation and boiled with an alkaline oxalate. The precipitated nickel oxalate is decomposed by boiling with sodium carbonate, producing sodium oxalate which may be used again, and nickel carbonate which is reduced by charcoal.

The uses of nickel have increased within the last few years. Dishes and crucibles of this metal have been used in the laboratory in many cases as substitutes for those of platinum and silver, though they are, of course, more easily oxidised. It has been found possible to weld sheet nickel upon iron and steel plates, and culinary vessels, &c., have been made of such plates, which are not liable to rust.

The pure metal is obtained by igniting the oxalate, as in the case of cobalt, which it much resembles in properties. It is a little heavier (sp. gr. 8.9) and rather more fusible.

The *oxides of nickel* correspond in composition to those of cobalt. The salts formed by nickelous oxide (NiO) are usually green, and give bright green solutions. The hydrate has a characteristic apple-green colour, and does not absorb oxygen from the air like the cobaltous hydrate. It dissolves in ammonia with a blue colour unchanged by air. The greater facility with which the cobalt is converted into sesquioxide has been applied (as above described) to effect the separation of the two metals. Nickelous oxide has been found native in octahedral crystals, which have also been obtained accidentally in a copper-smelting furnace.

Ni_3O_4 is obtained by passing moist oxygen over $NiCl_2$ at about 400° C. It has a metallic appearance, and is seen in octahedral crystals under the microscope. It is converted into NiO when heated, and dissolves in hydrochloric acid with evolution of chlorine.

Nickel sulphate ($NiSO_4.H_2O.6Aq$) forms fine green prismatic crystals, the water of constitution in which may be displaced by potassium sulphate, forming the *double sulphate of nickel and potassium*, $NiSO_4.K_2SO_4.6Aq$, which crystallises so readily that it was at one time the form in which nickel was separated from the other metals present in its ores.

Nickel sulphate may be obtained by dissolving nickel in dilute sulphuric acid. It is isomorphous with the sulphates of Mg, Zn, Fe, and Co. When ammonia is added to its solution, it produces a green precipitate of a basic salt, which dissolves in excess of ammonia to a violet solution, depositing violet crystals of $NiSO_4.4NH_3.2H_2O$.

Nickel-ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$, is used in electroplating with nickel. It is almost insoluble in ammonium sulphate.

Three *sulphides of nickel* are known—a *subsulphide*, Ni_2S; a *monosulphide*, NiS, found native as *capillary pyrites*, and obtained as a black precipitate by the action of an alkaline sulphide upon a salt of nickel: and a *disulphide*, NiS_2. Nickel sulphide, like cobalt sulphide, is insoluble in HCl; but ammonium disulphide dissolves it to a dark brown liquid.

Nickel is farther removed from iron than cobalt is; its peroxide, Ni_2O_3, shows no disposition to form salts, and it does not form any compound corresponding to ferro- or cobalti-cyanides. It has far less colouring power than cobalt, and its salts are commonly green. In many respects nickel more nearly resembles copper than iron.

MANGANESE.

$Mn'' = 55$ parts by weight.

230. Manganese much resembles iron in several particulars relating both to its physical and chemical characters, and is often found associated, in small quantities, with the compounds of that metal. It is found chiefly as *pyrolusite*, MnO_2, *braunite*, Mn_2O_3, and *manganese spar*, $MnCO_3$. The metal itself has not been applied to any useful purpose.

It is obtained by reducing manganous carbonate ($MnCO_3$) with charcoal, at a very high temperature, when a fused mass, composed of manganese combined with a little carbon (corresponding to cast-iron), is obtained, which is freed from carbon by a second fusion in contact with manganous carbonate.

Metallic manganese is grey with a red tinge, hard and brittle, sp. gr. 8, very difficult to fuse, and more easily oxidised than iron, so that it decomposes water when slightly warmed. It is only feebly attracted by the magnet.

Manganese dissolves easily in diluted hydrochloric or sulphuric acid, Mn displacing H_2, like Fe and Cr. It resembles iron in its tendency to combine with carbon at a high temperature to form a compound corresponding to cast-iron, and, in this form, the manganese is not oxidised by air.

The effect of an addition of manganese in improving the quality of melted or cast steel has long been known, but has not yet been clearly explained. Very little manganese is found in the steel itself, and it appears to act rather by purifying the steel from sulphur, phosphorus, and other substances.

Spiegel-eisen and *ferro-manganese* are alloys containing iron, manganese, and carbon, which are largely used in the production of Bessemer steel.

231. OXIDES OF MANGANESE, MnO, Mn_2O_3, Mn_3O_4, MnO_2, Mn_2O_7.

Manganese dioxide or *peroxide*, MnO_2, is the chief form in which this metal is found in nature, and is the source from which all other compounds of manganese are obtained. Its chief mineral form is *pyrolusite*, which forms steel-grey prismatic crystals of sp. gr. 4.8; but it is also found amorphous, as *psilomelane*, and in the hydrated state as *wad*. In commerce, pyrolusite is known as black manganese, or simply manganese, and is largely imported from Germany, Spain, &c., for the use of the manufacturer of bleaching-powder and the glass-maker. It is also used as a cheap source of oxygen, which it evolves when heated to redness, without fusing, leaving the *red oxide of manganese*, Mn_3O_4. The manganese dioxide is an indifferent oxide, and does not combine with acids. Strong HCl, however, dissolves it, giving a brown solution from which water precipitates a brown oxychloride. If the brown solution, which probably contains $MnCl_4$, be heated, it evolves Cl_2 and becomes colourless $MnCl_2$. Nitric acid is almost without action on it. Strong sulphuric acid evolves oxygen from it; $MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$. Even dilute sulphuric acid effects the same change if some substance ready to combine with oxygen is added, such as ferrous sulphate or oxalic acid. Hence a mixture of MnO_2 and H_2SO_4 is much used as an oxidising agent.

When heated in hydrogen, the oxides of manganese are not reduced to the metal, like those of iron, but are converted into MnO.

Manganous oxide, MnO, is a greenish powder obtained by heating MnO_2 or $MnCO_3$ in a current of hydrogen. It has been obtained in transparent emerald-green crystals. It easily absorbs oxygen from the air. It is a basic oxide, dissolving in acids to form the manganous salts. It has been found native in a manganiferous dolomite.

Manganic oxide, or *manganese sesquioxide*, Mn_2O_3, is found in the mineral *braunite* in octahedral crystals. By its general appearance it might be mistaken for MnO_2, but it dissolves in moderately strong sulphuric acid, forming a red solution of *manganic sulphate*, $Mn_2(SO_4)_3$.

Mn_2O_3 may be obtained by heating any of the oxides of manganese to redness in a current of oxygen, while Mn_3O_4 is formed when any one of the oxides is heated in air. When MnO_2 in very small quantity is added to melted glass, it imparts a purple colour, which is probably due to the formation of a manganic silicate. The amethyst is believed by some to owe its colour to the same cause.

Red oxide of manganese (Mn_3O_4) is the most stable of the oxides of this metal, and is formed when either of the others is heated in air. Thus obtained, it has a brown or reddish colour; but it is found in nature as the black mineral *hausmannite*. In composition it resembles the magnetic oxide of iron, but it seems probable that its true formula is $2MnO.MnO_2$, for when treated with diluted nitric acid it leaves the black hydrated dioxide. Strong sulphuric acid dissolves it to a red liquid containing manganous and manganic sulphates. Dilute sulphuric acid leaves MnO_2 undissolved. HCl dissolves it when heated, evolving Cl and leaving $MnCl_2$.

Permanganic anhydride, Mn_2O_7, is a red oily liquid formed when potassium permanganate is decomposed by strong sulphuric acid; $K_2Mn_2O_8 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O$.

It decomposes slowly, even at common temperatures, evolving oxygen, together with violet vapour of Mn_2O_7. When heated, it decomposes with explosion. It is a most powerful oxidising agent, setting fire to most combustible bodies. In contact with water, it yields *permanganic acid*, $H_2Mn_2O_8$.

Manganous hydrate, $Mn(OH)_2$, is obtained as a white precipitate when an alkali is added to a manganous salt, out of contact with air. When exposed to air, it rapidly becomes brown, forming manganic hydrate.

Manganic hydrate, $Mn_2O_2(OH)_2$, may be regarded as Mn_2O_3, in which O has been replaced by $(OH)_2$, or as $Mn_2O_3.H_2O$, hydrated manganese sesquioxide. It is found in dark grey prismatic crystals, as *manganite*, associated with MnO_2, from which it differs by giving a brown instead of a black streak on unglazed earthenware. Moreover, on boiling it with dilute nitric acid, part of it is dissolved as manganous nitrate, leaving a hydrated manganese dioxide, which dissolves to a brown solution when thoroughly washed. A hydrated manganese dioxide is also precipitated when chloride of lime is added to a manganous salt.

Manganic acid, H_2MnO_4, has not been obtained, but several manganates are known, which are isomorphous with the chromates and sulphates.

Potassium manganate, K_2MnO_4, is formed when MnO_2 is fused with potash; $3MnO_2 + 2KHO = K_2MnO_4 + Mn_2O_3 + H_2O$. If an oxidising agent, such as air or nitre, be present, the Mn_2O_3 is also converted into K_2MnO_4; $Mn_2O_3 + 4KHO + O_3 = 2K_2MnO_4 + 2H_2O$. The extraction of oxygen from air upon this principle has been described at p. 33.

Sodium manganate (Na_2MnO_4), obtained by heating manganese dioxide with sodium hydrate under free exposure to air, is employed in a state of solution in water, as *Condy's green disinfecting fluid*. It is also used as a bleaching agent, and in the preparation of oxygen at a cheap rate. The manganates of potassium and sodium dissolve in water containing potash or soda, forming green liquids, but when dissolved in pure water, they are decomposed, yielding the red permanganates—

$$3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaHO.$$

Barium manganate forms the pigment known as *Cassel green*.

Permanganic acid, $H_2Mn_2O_8$, has been obtained in a hydrated crystalline state by decomposing the barium permanganate with sulphuric acid, and evaporating the solution *in vacuo*. It is a brown substance, easily dissolving in water to a red liquid, which is decomposed at about 90° F., evolving oxygen, and depositing manganese dioxide.

Potassium permanganate, $K_2Mn_2O_8$, forms rhombic prisms isomorphous with the perchlorate, $KClO_4$, on which account it is sometimes written $KMnO_4$. It dissolves in 16 parts of cold water, forming a purple solution, which becomes green K_2MnO_4 by contact with many substances capable of taking up oxygen. When crystallised permanganate is heated to 240° C. it gives manganate—

$$K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2.$$

It is largely used in many chemical operations. In order to prepare it, 4 parts of finely powdered manganese dioxide are intimately mixed with $3\frac{1}{2}$ parts of potassium chlorate, and 5 parts of potassium hydrate dissolved in a very little water. The pasty mass is dried, and heated to dull redness for some time in an iron tray or earthen crucible. The potassium chlorate imparts the required oxygen. On treating the cold mass with water, potassium manganate is dissolved, forming a dark green solution. This is diluted with water, and a stream of carbonic acid gas passed through it as long as any change of colour is observed; $3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + MnO_2 + 2K_2CO_3$. The precipitated MnO_2 is allowed to settle, and the clear red solution poured off and evaporated to a small bulk. On cooling, it deposits prismatic crystals of the permanganate ($K_2Mn_2O_8$), which are red by transmitted light, but reflect a dark green colour. The potassium carbonate, being much more soluble in water, is left in the solution. Potassium permanganate is remarkable for its great colouring power, a very small quantity of the salt producing an intense purplish-red colour in a large quantity of water. Its solution in water is very easily decomposed and bleached by substances having an attraction for oxygen, such as sulphurous acid or a ferrous salt. If a very small piece of iron wire be dissolved in diluted sulphuric acid, the solution of ferrous sulphate so produced will decolorise a large volume of weak solution of the permanganate, being converted into ferric sulphate—

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

This decomposition forms the basis of a valuable method for determining the proportion of iron in its ores.

Many organic substances are easily oxidised by potassium permanganate, and this is the case especially with the offensive emanations from putrescent organic matter. Hence it is extensively used, under the name of *Condy's red disinfecting fluid*, in cases where a solid or liquid substance is to be deodorised.

An alkaline solution of the permanganate is sometimes used as an oxidising agent, since it parts with oxygen when boiled, becoming green from the production of manganate—

$$K_2Mn_2O_8 + 2KHO = 2K_2MnO_4 + H_2O + O.$$

Sodium permanganate, $Na_2Mn_2O_8$, is often used as a disinfectant, being cheaper than the potassium salt. It is made by heating MnO_2 with NaHO, in a flat vessel, exposed to air, for 48 hours, to dull redness; the mass is boiled with water to convert the manganate into permanganate; $3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaHO$.

232. CHLORIDES OF MANGANESE.—There appear to be three compounds of manganese with chlorine, corresponding to three of the oxides, viz., $MnCl_2$, Mn_2Cl_6, and $MnCl_4$; but only the first is obtainable in the pure state, the others forming solutions which are easily decomposed with evolution of chlorine.

By dissolving potassium permanganate in oil of vitriol, and adding fragments of fused sodium chloride, a remarkable greenish-yellow gas is obtained, which gives purple fumes with moist air, and is decomposed by water, yielding a red solution which contains hydrochloric and permanganic acids. It, therefore, must contain manganese and chlorine, and is sometimes regarded as the perchloride ($MnCl_4$); but it is more probably an oxychloride of manganese (see *Chlorochromic acid*). Care is required in its preparation, which is sometimes attended with explosion.

The *manganous chloride* ($MnCl_2$) is obtained in large quantity as a waste product in the preparation of chlorine for the manufacture of bleaching-powder. Since there is no useful application for it, the manufacturer sometimes reconverts it into the black oxide. As the native binoxide always contains iron, the liquor obtained by treating it with hydrochloric acid contains ferric chloride (Fe_2Cl_6) mixed with chloride of manganese ($MnCl_2$). In order to separate the iron, advantage is taken of the circumstance that sesquioxides are weaker bases than the protoxides, so that if a small proportion of lime or chalk be added to the solution, the iron may be precipitated as ferric oxide, without decomposing the chloride of manganese; $Fe_2Cl_6 + 3CaO = Fe_2O_3 + 3CaCl_2$.

After separating the Fe_2O_3, *an excess* of lime is added and air blown through the mixture at about 150° F., when the white precipitate of MnO, formed at first, absorbs the oxygen, and becomes a black compound of MnO_2 with lime, which is used over again for the preparation of chlorine. Unless the lime is added in excess, only $MnO.MnO_2$ is formed, so that the excess of lime displaces the MnO and allows it to be converted into MnO_2. In another process Weldon employs magnesia instead of lime, with the view of afterwards recovering the chlorine from the chloride of magnesium, in the form of hydrochloric acid (see p. 289), and using the magnesia over again.

Manganous sulphate, $MnSO_4.H_2O.6Aq$, isomorphous with green vitriol, forms faint pink crystals easily soluble in water. It is prepared by adding strong sulphuric acid to manganese dioxide, heating the paste to redness to decompose any ferric sulphate, extracting with water, precipitating the last traces of iron by adding manganous carbonate, filtering, and crystallising. Manganous sulphate is employed by the dyer and calico-printer in the production of black and brown colours. Crystals have been obtained of $MnSO_4.H_2O.4Aq$.

Manganous sulphide, MnS, occurs as *manganese blende* in steel-grey masses. It may be obtained as a greenish powder by heating any of the oxides of manganese in a current of H_2S. When precipitated by alkaline sulphides from manganese salts, it has a pink colour and contains water. When the pink precipitate is boiled with an excess of alkaline sulphide, it becomes a green crystalline powder, $3MnS.H_2O$. The manganous sulphide has a tendency to form soluble compounds with the alkaline sulphides, so that a solution of manganese often requires boiling with ammonium sulphide before a precipitate is formed. Manganous sulphide dissolves easily in dilute HCl.

Manganese disulphide, MnS_2, is found, in crystals belonging to the regular system, as *Hauerite*, in Hungary.

Manganese, though more nearly allied to iron than to any other metal, is parted from it by the greater stability of the manganous salts, which are less easily oxidised than the ferrous salts, as well as by the far greater stability of the manganates and by the existence of permanganates which have no parallel in the iron series.

CHROMIUM.

Cr = 52.5 parts by weight.

233. This metal derives its name from *χρῶμα*, *colour*, in allusion to the varied colours of its compounds, upon which their uses in the arts chiefly depend. It is comparatively seldom met with, its principal ore being the *chrome-iron ore* ($FeO.Cr_2O_3$), which is remarkable for its resistance to the action of acids and other chemical agents.* It is chiefly found in the Shetland Islands, Sweden, Russia, Hungary, and the United States, and is imported for the manufacture of *bichromate of potash* ($K_2O.2CrO_3$), which is one of the chief commercial compounds of chromium. The ore is first heated to redness and thrown into water, in order that it may be easily ground to a fine powder, which is mixed with carbonate of potash, chalk being added to prevent the fusion of the mass, and strongly heated in a current of air on the hearth of a reverberatory furnace, the mass being occasionally stirred to expose a fresh surface to the air. The ferrous oxide is thus converted into ferric oxide, and the oxide of chromium (Cr_2O_3) into potassium chromate (K_2CrO_4); $2(FeO.Cr_2O_3) + 4K_2CO_3 + O_7 = Fe_2O_3 + 4K_2CrO_4 + 4CO_2$. Nitre is sometimes added to hasten the oxidation. On treating the mass with water, a yellow solution of potassium chromate is obtained, which is drawn off from the insoluble residue of ferric oxide and lime, and mixed with a slight excess of nitric acid—

$$2(K_2CrO_4) + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

The solution, when evaporated, deposits beautiful red tabular crystals of bichromate of potash (potassium dichromate) which dissolve in 10 parts of cold water, forming an acid solution. It is from this salt that the other compounds of chromium are immediately derived.

Metallic chromium has received no useful application. It is obtained by reducing chromic chloride with zinc at a high temperature, and removing the excess of zinc with dilute nitric acid. It has a grey colour, is about as heavy as iron (sp. gr. 7.3), is extremely hard, and less fusible than platinum. It resembles aluminium in not being acted on by nitric acid, but HCl dissolves it, yielding chromous chloride, $CrCl_2$, a property which connects chromium with iron. Chromium, like aluminium, is attacked by the alkaline hydrates at high temperatures, evolving hydrogen and producing chromates. By the action of sodium on chromic chloride, the metal has been obtained in octahedral crystals, which are not dissolved by nitrohydrochloric acid.

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* There appear to be four types of chrome-iron ore, viz., $FeO.Cr_2O_3$, $2FeO.Cr_2O_3$, $3FeO.2Cr_2O_3$, and $2FeO.3Cr_2O_3$.

234. OXIDES OF CHROMIUM.—Three oxides of chromium are known in the separate state—*chromic oxide*, Cr_2O_3, *chromium dioxide*, CrO_2, and *chromic anhydride*, CrO_3. *Monoxide of chromium* or *chromous oxide* (CrO) is known in the hydrated state, and *perchromic acid* ($H_2Cr_2O_8$) is believed to exist in solution. The chromous salts correspond to the ferrous salts, but are much more susceptible of oxidation.

Chromic anhydride (often called *chromic acid*), the most important of these, is obtained by adding to one measure of a solution of potassium dichromate, saturated at 130° F., one measure and a half of concentrated sulphuric acid, by small portions at a time, and allowing the solution to cool, when chromic anhydride crystallises out in fine crimson needles, which are deliquescent, very soluble in water, fusing easily, and decomposed at 250° C. into oxygen and chromic oxide. Chromic anhydride is a powerful oxidising agent; most organic substances, even paper, will reduce it to the green chromic oxide. A mixture of potassium dichromate and sulphuric acid is employed for bleaching some oils, the colouring matter being oxidised at the expense of the chromic acid, and chromic sulphate produced—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + O_3 + 4H_2O.$$

The dichromate itself evolves oxygen when heated to bright redness, being first fused, and afterwards decomposed; $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. Heated with strong HCl, it evolves Cl; $K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + Cl_6$. The oxidising effect of the potassium dichromate, under the action of light, upon gelatin and albumen, receives very important applications in photography.

Sodium dichromate, $Na_2Cr_2O_7$, is much more soluble than the potassium salt, requiring only an equal weight of water; it is now often substituted for potassium dichromate.

Chromic acid, H_2CrO_4, is not known in the pure form. Its salts, the chromates, are isomorphous with the sulphates.

Chromate of potash, or *normal potassium chromate* ($K_2O.CrO_3$ or K_2CrO_4), is formed by adding potassium carbonate to the red solution of potassium dichromate until its red colour is changed to a fine yellow, when it is evaporated and allowed to crystallise. It forms yellow prismatic crystals, having the same form as those of potassium sulphate, and is five times as soluble in water as the dichromate, yielding an alkaline solution, which is partly decomposed by evaporation, with formation of the dichromate. Acids, even carbonic, change its solution from yellow to red, from production of dichromate. It becomes red when heated, and yellow again on cooling, and fuses without decomposition. Potassium chromate has been found in some yellow samples of saltpetre from Chili. No compound corresponding to $KHSO_4$ is known.

Trichromate of potash ($K_2O.3CrO_3$) has been obtained in red crystals by adding nitric acid to the dichromate.

It will be observed that the chromates of potassium are rather exceptional salts. The yellow or normal chromate, K_2CrO_4, is formed upon the model of *imaginary* chromic acid, H_2CrO_4. The red chromate, or potassium dichromate, is not a true acid salt, for it contains no hydrogen; it is sometimes called *anhydro-chromate*, and written $K_2CrO_4.CrO_3$. The trichromate would be $K_2CrO_4.2CrO_3$.

Barium chromate, $BaCrO_4$, is used in painting, as *yellow ultramarine*, being precipitated by potassium chromate from barium chloride; it is insoluble in acetic acid.

Chrome-yellow is the *chromate of lead* ($PbCrO_4$), prepared by mixing dilute solutions of lead acetate and potassium chromate. The precipitate is insoluble in acetic acid. It is largely used in painting and calico-printing, and by the chemist as a source of oxygen for the analysis of organic substances, since, when heated, it fuses to a brown mass, which evolves oxygen at a red heat. Chrome-yellow being a poisonous salt, its occasional use for colouring confectionery is very objectionable. Chromate of lead in prismatic crystals forms the rather rare *red lead ore of Siberia*, in which chromium was first discovered.

Orange chrome is a *basic chromate of lead* ($PbCrO_4.PbO$), and may be obtained by boiling the yellow chromate with lime; $2(PbCrO_4) + CaO = PbCrO_4.PbO + CaCrO_4$. The calico-printer dyes the stuff with yellow chromate of lead, and converts it into orange chromate by a bath of lime-water. Chrome-orange is also made by precipitating a lead salt with a weak alkaline solution of potassium chromate, which gives a mixture of the two chromates of lead.

Silver chromate, Ag_2CrO_4, is obtained as a red crystalline precipitate when silver nitrate is added to potassium chromate.

When potassium dichromate is added gradually to silver nitrate, a scarlet precipitate of *silver dichromate*, $Ag_2Cr_2O_7$, is obtained; and if this be boiled with water, it leaves Ag_2CrO_4 in dark green crystals, which become red when powdered.

The colour of the *ruby* (crystallised alumina) appears to be due to the presence of a small proportion of chromic anhydride.

Sesquioxide of chromium, or *chromic oxide* (Cr_2O_3), is valuable as a green colour, especially for glass and porcelain, since it is not decomposed by heat. Being extremely hard, it is used in making razor-strops. It is prepared by heating potassium dichromate with one-fourth of its weight of starch, the carbon of which removes oxygen, leaving a mixture of chromic oxide with potassium carbonate, which may be removed by washing with water. If sulphur be substituted for the starch, potassium sulphate will be formed, which may also be removed by water. When chromic oxide is strongly heated, it exhibits a sudden glow, becomes darker in colour, and insoluble in acids which previously dissolved it easily; in this respect it resembles alumina and ferric oxide. Like these oxides, the chromic oxide is a feeble base; it is remarkable for forming two classes of salts, having the same composition, but differing in the colour of their solutions, and in some other properties. Thus, there are two modifications of the *chromic sulphate*—the green sulphate, $Cr_2(SO_4)_3.5Aq$, and the violet sulphate, $Cr_2(SO_4)_3.15Aq$. The solution of the latter becomes green when boiled, being converted into the former. *Chrome alum* forms dark purple octahedra ($KCr'''(SO_4)_2.12Aq$) which contain the violet modification of the sulphate; and if its solution in water be boiled, its purple colour changes to green, and the solution refuses to crystallise. It is obtained as a secondary product in certain chemical manufactures, and may be prepared by the action of sulphurous acid gas on a mixture of potassium dichromate and sulphuric acid; $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O$.* The anhydrous chromic sulphate forms red crystals, which are insoluble in water and acids. A green basic *chromic borate* is used in painting and calico-printing, under the name of *vert de Guignet*, and is prepared by strongly heating potassium dichromate with 3 parts of crystallised boric acid, when potassium borate and chromic borate are formed, oxygen being expelled. The potassium borate and the excess of B_2O_3 are afterwards washed out by water. Cr_2O_3 combines with the oxides of the magnesium group of metals to form very insoluble and infusible compounds, crystallising in octahedra, *e.g.*, $ZnO.Cr_2O_3$, $MnO.Cr_2O_3$, $FeO.Cr_2O_3$.

Chromic hydrate, $Cr_2(HO)_6$, is thrown down by alkalies from solutions of chromic salts, such as chrome alum, as a greenish-blue precipitate. It dissolves sparingly in ammonia to a pink solution, from which chromic oxide is precipitated by boiling. Potash dissolves it to a fine green solution which becomes gelatinous when boiled, from precipitation of chromic oxide.

Chromium dioxide, CrO_2.—When potassium dichromate is reduced by nitric oxide or sodium thiosulphate, a brown precipitate is obtained; this is a compound of water with CrO_2, which is left, on heating to 250° C., as a black powder which evolves oxygen at 300° C., becoming Cr_2O_3.

Chromous oxide (CrO) is not known in the pure state, but is precipitated as a brown hydrate when chromous chloride is decomposed by potash. It absorbs oxygen even more readily than ferrous oxide, becoming converted into $CrO.Cr_2O_3$, corresponding in composition to the magnetic oxide of iron. Chromous oxide is a feeble base; a double sulphate, $K_2Cr''(SO_4)_2.6Aq$, is known, which has the same crystalline form as the corresponding iron salt, $K_2Fe''(SO_4)_2.6Aq$; it has a blue colour, and gives a blue solution, which becomes green when exposed to air, from the formation of chromic oxide.

Perchromic acid ($H_2Cr_2O_8$) is believed to exist in the blue solution obtained by the action of hydric peroxide upon solution of chromic acid, but neither the acid nor its salts have been obtained in a separate state (see p. 56).

235. CHLORIDES OF CHROMIUM.—The *chromic chloride* (Cr_2Cl_6) obtained by passing dry chlorine over a mixture of chromic oxide with charcoal, heated to redness in a glass tube, is converted into vapour, and condenses upon the cooler part of the tube in shining leaflets having a fine violet colour. When heated in air, it is decomposed, evolving Cl, and leaving Cr_2O_3. Very soluble green crystals of $Cr_2Cl_6.12Aq$ may be obtained, but the water cannot be expelled without decomposing the chloride. Cold water does not affect Cr_2Cl_6, but boiling water slowly dissolves it to a green solution resembling that obtained by dissolving chromic oxide in hydrochloric acid.

Chromous chloride ($CrCl_2$) results from the action of hydrogen. at a red heat, upon chromic chloride. Strange to say, it is white, and dissolves in water to form a blue solution, which absorbs oxygen from the air, becoming green. It is remarkable that if the violet chromic chloride is suspended in water, and a minute quantity of chromous chloride added, the former immediately dissolves to a green solution, evolving heat. $CrCl_2$ is also formed when chromium is dissolved in HCl. A solution of chromic chloride or sulphate, mixed with HCl, is reduced to chromous chloride by metallic zinc, the liquid becoming greenish blue and giving a pink precipitate of chromous acetate on addition of ammonium acetate, becoming blue when shaken with air. Chromous chloride resembles ferrous chloride in absorbing NO to form a brown compound.

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* Exposure to cold, it is said, again converts it into the crystallisable violet form.

Chromyle chloride, CrO_2Cl_2 (= 2 vols.), or chromic oxychloride, formerly called *chlorochromic acid*, bears the same relation to CrO_3 as sulphuryle chloride, SO_2Cl_2, does to SO_3. It is a very remarkable brown-red liquid, obtained by distilling 10 parts of common salt and 17 of potassium dichromate previously fused together and broken into fragments, with 40 parts of oil of vitriol—

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrO_2Cl_2.$$

It much resembles bromine in appearance, and fumes very strongly in air, the moisture of which decomposes its red vapour, forming chromic and hydrochloric acids; $CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$. Its sp. gr. is 1.92, and it boils at 118° C. It is a very powerful oxidising and chlorinating agent, and inflames ammonia and alcohol when brought in contact with them.

It is occasionally used to illustrate the nature of illuminating flames; for if hydrogen be passed through a bottle containing a few drops of it, the gas becomes charged with its vapour, and, if kindled, burns with a brilliant white flame, which deposits a beautiful green film of chromic oxide upon a cold surface. When heated, in a sealed tube, to 190° C., it is converted into a black solid body, according to the equation $3CrO_2Cl_2 = Cl_4 + CrCl_2.2CrO_3$. When potassium dichromate is gently warmed with HCl, the solution deposits red prisms of $KClCrO_3$, formerly known as *potassium chlorochromate*, which may be regarded as $CrO_2Cl(KO)$, being derived from the at present unknown $CrO_2Cl(HO)$, corresponding to $SO_2Cl(HO)$.

Chromyle fluoride, CrO_2F_2, formerly believed to be *chromic fluoride* (CrF_6), is another volatile compound of chromium obtained by distilling lead chromate with fluor spar and sulphuric acid; it is a red gas, condensible to a red liquid at a low temperature. Water decomposes it, yielding chromic and hydrofluoric acids.

Chromic sulphide (Cr_2S_3) is formed when vapour of carbon disulphide is passed over chromic oxide heated to redness. It forms black lustrous scales resembling graphite.

By fusing chromic hydrate with sodium carbonate and sulphur, *sodium sulphochromite*, $Na_2Cr_2S_4$, is obtained, as a dark red body insoluble in water, and not easily attacked by hydrochloric or sulphuric acid. Sulphochromites of other metals have also been obtained.

Chromium nitride, CrN, has been obtained by heating chromium to redness in nitrogen.

Chromium is nearly allied to iron by its property of forming chromous and chromic salts, and to manganese through the chromates which correspond and are isomorphous with the manganates, and rival them in colour.

236. *General review of iron, cobalt, nickel, manganese, and chromium.*—Many points of resemblance will have been noticed in the chemical history of these metals. They are all capable of decomposing water at a red heat, and easily displace hydrogen from hydrochloric acid. Each of them forms a base by combining with one atom of oxygen, and these oxides produce salts which have the same crystalline form. All these oxides, except that of nickel, easily absorb oxygen from the air, and are converted into sesquioxides. The sesquioxide of nickel is an indifferent oxide, while that of cobalt is very feebly basic; the sesquioxide of manganese is a stronger base, and the basic properties of the sesquioxides of chromium and iron are very decided. Nickel does not exhibit any tendency to form a well-marked acid oxide, but the existence of an acid oxide of cobalt is suspected; and iron, manganese, and chromium form undoubted acid oxides with three atoms of oxygen. Nickel is only known to form one compound with chlorine; cobalt and manganese form, in addition to their protochlorides, very unstable perchlorides

known only in solution, but iron and chromium form very stable volatile perchlorides. The metals composing this group are all diatomic,* and are found associated in natural minerals; this is especially the case with iron, manganese, cobalt, and nickel. They are all attracted by the magnet, and require a very high temperature for their fusion. Iron and chromium connect this group with aluminium, their sesquioxides being isomorphous with alumina, and their perchlorides volatile like aluminium chloride.

237. MOLYBDENUM (Mo=96) derives its name from *μολύβδαινα*, *lead*, on account of the resemblance of its chief ore, *molybdena*, to black lead. Molybdena, or *molybdenum glance*, is the *molybdenum disulphide* (MoS_2), and is found chiefly in Bohemia and Sweden; it may be recognised by its remarkable similarity to plumbago, and by its giving a blue solution when boiled with strong sulphuric acid. It is chiefly employed for the preparation of ammonium molybdate, which is used in testing for phosphoric acid. For this purpose the disulphide is roasted in air at a dull red heat, when SO_2 is evolved, and *molybdic anhydride* (MoO_3) mixed with oxide of iron is left. The residue is digested with strong ammonia, which dissolves the former as *ammonium molybdate*, obtainable in prismatic crystals (NH_4HMoO_4) on evaporation. When a solution of ammonium molybdate is added to a phosphate dissolved in diluted nitric acid, a yellow precipitate of *ammonium phosphomolybdate* is produced, which contains molybdic and phosphoric acids combined with ammonia, by the formation of which very minute quantities of phosphoric acid can be detected. If hydrochloric acid be added in small quantity to a strong solution of molybdate of ammonium, the molybdic acid is precipitated, but it is dissolved by an excess of hydrochloric acid, and if the solution be dialysed, the molybdic acid is obtained in the form of an aqueous solution which reddens blue litmus, has an astringent taste, and leaves a soluble gum-like residue when evaporated. Molybdic anhydride fuses at a red heat to a yellow glass, and may be sublimed in a current of air in shining needles. In contact with diluted hydrochloric acid and metallic zinc, it is converted into a blue compound of the composition $MoO_2.4MoO_3$, which is soluble in water, but is precipitated on adding a saline solution. *Molybdate of lead* ($PbMoO_4$) is found as a yellow crystalline mineral. The *molybdic oxide* (MoO_2) is basic, and forms dark red-brown salts. *Molybdous oxide* (MoO) is obtained by adding an alkali to the solution resulting from the prolonged action of zinc upon a hydrochloric solution of molybdic acid. It is a basic oxide which absorbs oxygen from the air.

Metallic molybdenum is obtained by reducing molybdic anhydride with charcoal at a white heat, as a white metal, fusible with difficulty, unacted upon by hydrochloric and diluted sulphuric acids, but converted into molybdic acid by boiling with nitric acid. It is rather a light metal, its specific gravity being 8.62. When heated in chlorine it yields *molybdenum tetrachloride* ($MoCl_4$), which forms a red vapour, and condenses in crystals resembling iodine, soluble in water. A *dichloride* ($MoCl_2$) and *pentachloride* ($MoCl_5$) are also known. The *trisulphide* (MoS_3) and *tetrasulphide* (MoS_4) of molybdenum are soluble in alkaline sulphides.

In addition to the natural sources of molybdenum above mentioned, there may be noticed *molybdic ochre* (an impure molybdic anhydride), and the difficultly fusible masses called *bear*, from the copper works in Saxony, which contain a large amount of molybdenum combined with iron, copper, cobalt, and nickel. Molybdenum has been detected in the mud deposited by the Buxton thermal water.

238. VANADIUM † (V=51.3) was originally discovered in certain Swedish iron ores, but its chief ore is the *vanadate of lead*, which is found in Scotland, Mexico, and Chili. Vanadic acid has also been found in some clays, in the cupriferous sandstone at Perm in Russia, and Alderley Edge in Cheshire. By treating the vanadate of lead with nitric acid, expelling the excess of acid by evaporation, and washing out the lead nitrate with water, impure *vanadic anhydride* (V_2O_5) is obtained, which may be purified by dissolving in ammonia, crystallising the vanadate of ammonium, and decomposing it by heat, when vanadic anhydride is left as a reddish-yellow fusible solid which crystallises on cooling, and dissolves

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* Chromium, like iron, is triatomic in the sesquioxides and the compounds derived from it, and in chromic acid it must be regarded as hexatomic.

† *Vanadis*, a Scandinavian deity.

sparingly in water, giving a yellow solution. It dissolves in hydrochloric acid, and if the solution be treated with a reducing agent (such as hydrosulphuric acid) it assumes a fine blue colour. If a solution of ammonium vanadate be mixed with tincture of galls, it gives an intensely black fluid, which forms an excellent ink, for it is not bleached by acids (which turn it blue), alkalies, or chlorine.

Vanadium itself has been obtained by heating its chloride in hydrogen, as a silvery white metal. Berzelius endeavoured to procure it by heating vanadic acid with potassium, but Roscoe, who has carefully investigated the vanadium compounds, has shown that the apparently metallic powder thus obtained is really an oxide (V_2O_2).

239. The oxides of vanadium correspond in composition to those of nitrogen. V_2O_2 is a basic oxide forming salts which give lavender-coloured solutions; these absorb oxygen rapidly from the air, and act as powerful reducing agents. V_2O_3 is a black crystalline body resembling plumbago, and capable of conducting electricity, obtained by heating vanadic anhydride in a current of hydrogen; it is a basic oxide. V_2O_4 is produced when V_2O_3 is heated in air; it also plays the part of a base, yielding blue salts. Vanadic anhydride, V_2O_5, forms purple and green compounds with the above oxides. *Metavanadic acid*, HVO_3, crystallises in beautiful golden scales. The yellow fuming liquid formerly called chloride of vanadium is really an oxychloride, $VOCl_3$. The oxychlorides, V_2O_2Cl, $VOCl$, and $VOCl_2$, have also been obtained. There are two compounds of vanadium with nitrogen, VN and VN_2. It will be remarked that the composition of the compounds of vanadium connects this metal with nitrogen, phosphorus, and arsenic. Compounds of vanadium are now used for blacks in calico-printing, in conjunction with chlorates and aniline hydrochlorate. The slag of the Creusot steel works is now the chief source of vanadic acid, of which it contains 2 per cent.

BISMUTH.

$Bi''' = 210$ parts by weight.

240. Bismuth, though useful in various forms of combination, is too brittle to be employed in the pure metallic state. It is readily distinguished from other metals by its peculiar reddish lustre and its highly crystalline structure, which is very perceptible upon a freshly broken surface; large cubical (or, strictly speaking, rhombohedral) crystals of bismuth are easily obtained by melting a few ounces in a crucible, allowing it to cool till a crust has formed upon the surface, and pouring out the portion which has not yet solidified, when the crystals are found lining the interior of the crucible. It is isomorphous with antimony. It is somewhat lighter than lead (sp. gr. 9.8), and volatilises more readily at high temperatures. It is less volatile than antimony, and burns like it in air.

Unlike most other metals, bismuth is found chiefly in the metallic state, disseminated in veins, through gneiss and clay-slate. The chief supply is derived from the mines of Schneeberg, in Saxony, where it is associated with the ores of cobalt. Native bismuth, together with the oxides and sulphides, is found abundantly in Bolivia, accompanied by tin-stone and sometimes by silver and gold; and the metal, the carbonate, and the sulphide have been lately found in France, in Colorado, and in Utah.

In order to extract the metal from the masses of earthy matter through which it is distributed, advantage is taken of its very low fusing point (264° C.). The ore is broken into small pieces, and introduced into iron cylinders which are fixed in an inclined position over a furnace (fig. 245). The upper opening of the cylinders, through which the ore is introduced, is provided with an iron door, and the lower opening is closed with a plate of firebrick perforated for the escape of the metal, which flows out, when the cylinders are heated, into iron receiving pots, which are kept hot by a charcoal fire.

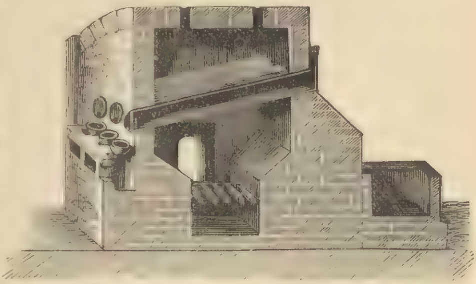

Fig. 245.—Extraction of bismuth.

Commercial bismuth generally contains considerable quantities of arsenic, sulphur, and silver; it is sometimes *cupelled* in the same manner as lead, in order to extract the silver, the oxide of bismuth being afterwards again reduced to the metallic state by heating it with charcoal. Pure bismuth dissolves entirely and easily in diluted nitric acid (sp. gr. 1.2); but if it contains arsenic, a white deposit of bismuth arsenate is obtained. Hydrochloric and diluted sulphuric acids will not act upon bismuth.

The chief use of bismuth is in the preparation of certain alloys with other metals. Some kinds of type metal and stereotype metal contain bismuth, which confers upon them the property of expanding in the mould during solidification, so that they are forced into the finest lines of the impression.

This metal is also remarkable for its tendency to lower the fusing point of alloys, which cannot be accounted for merely by referring to the low fusing point of the metal itself. Thus, an alloy of 2 parts bismuth, 1 part lead, and 1 part tin, fuses below the temperature of boiling water, although the most fusible of the three metals, tin, requires a temperature of 228° C. An alloy of this kind is used for soldering pewter. Bismuth is also employed, together with antimony, in the construction of thermo-electric piles.

241. OXIDES OF BISMUTH.—There are four oxides, Bi_2O_2, Bi_2O_3, Bi_2O_4, and Bi_2O_5. *Bismuthous oxide* (Bi_2O_2) is obtained as a black precipitate when bismuthic chloride mixed with stannous chloride is added to excess of potash.

(1) $2BiCl_3 + SnCl_2 = Bi_2Cl_4 + SnCl_4$; (2) $Bi_2Cl_4 + 4KHO = Bi_2O_2 + 4KCl + 2H_2O$.

It acts as a weak base. Exposed to air when moist, it becomes Bi_2O_3. Heat has the same effect on the dry oxide.

Bismuthic oxide (Bi_2O_3) is the basic and most important oxide of the metal. It is formed when bismuth is heated in air, or when bismuth nitrate is decomposed by heat, and is a yellow powder which becomes brown when heated, and fuses easily. Bismuthic oxide forms the rare mineral *bismuth-ochre*. Bi_2O_3 is obtained in fine needles by precipitating a boiling solution of a bismuth salt with potash.

Bismuthic anhydride (Bi_2O_5) is formed when bismuthic oxide is suspended in a strong solution of potash through which chlorine is passed, when a brown substance is formed which, when treated with warm strong nitric acid, yields bismuthic acid ($HBiO_3$) as a red powder, which becomes brown at 120° C., losing H_2O and becoming Bi_2O_5. When further heated, this loses O and becomes Bi_2O_4 or $Bi_2O_3.Bi_2O_5$. When heated with acids it also evolves oxygen, and forms salts of bismuthic oxide. The bismuthates of the alkali metals are very unstable, being decomposed by water.

Bismuth hydrate, $Bi(OH)_3$, is obtained as a white precipitate when a caustic alkali is added to a bismuth salt; it does not dissolve in excess of alkali. Acted on by chlorine in the alkaline liquid, it becomes dark brown bismuthic hydrate or acid.

Bismuthic acid, $HBiO_3$, is formed when basic bismuth nitrate is fused with potash, in contact with air, until it has become dark brown. On dissolving in dilute nitric acid, $HBiO_3$ is left as a red powder. The bismuthates of the alkali metals are very unstable, being decomposed by water. *Pyrobismuthic acid*, $H_4Bi_2O_7$, is said to have been obtained.

242. The only two salts of bismuth which are known in the arts are the *basic nitrate* (*trisnitrate of bismuth* or *flake-white*) and the *oxychloride of bismuth* (*pearl-white*). The preparation of these compounds illustrates one of the characteristic properties of the salts of bismuth, viz., the facility with which they are decomposed by water with the production of insoluble basic salts.

If bismuth be dissolved in nitric acid, it becomes bismuthic nitrate, $Bi(NO_3)_3$, and this may be obtained in prismatic crystals containing 5Aq. If the solution be mixed with a large quantity of water, it deposits a precipitate of *flake-white*, $Bi(NO_3)_3.2Bi(OH)_3$, or $Bi(OH)_2NO_3$, the remainder of the nitric acid being left in the solution—

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3.$$

The basic nitrate, when long washed, becomes $Bi(OH)_3$. It is a crystalline powder, which is acid to moist test-paper. It is used as a paint and cosmetic, and in enamelling porcelain.

Pearl-white has the composition 6BiOCl.Aq, and is obtained by dissolving bismuth in nitric acid, and pouring the solution into water in which common salt has been dissolved.

Bismuthite, which is, next to native bismuth, the most important of the bismuth ores, is composed of $3Bi_2O_3.CO_2.H_2O$.

Bismuthic chloride, $BiCl_3$ (=2 vols.), may be distilled over when bismuth is heated in a current of dry chlorine; it is a deliquescent, fusible, volatile, crystalline solid, easily dissolved by a small quantity of water, but decomposed by much water, with formation of the above-mentioned *oxychloride of bismuth;* $BiCl_3 + H_2O = BiOCl + 2HCl$. This compound is so insoluble in water that nearly every trace of bismuth may be precipitated from a moderately acid solution of the trichloride by adding much water.

Bismuth tri-iodide, BiI_3, is obtained as a dark brown precipitate when potassium iodide is added to a solution of a bismuthic salt. If the solution be dilute or very acid, a red or yellow colour is produced, without precipitation, and if a solution of a lead salt be added to this, a brown or red precipitate of a double iodide of bismuth and lead is produced, which dissolves in hot dilute HCl, and separates in minute crystals like bronze powder on cooling.

Bismuthous sulphide (Bi_2S_2) is sometimes found in nature, but more frequently *bismuthic sulphide* (Bi_2S_3) or *bismuth glance*, which occurs in dark grey lustrous prisms isomorphous with native sulphide of antimony. It is also obtained as a brown precipitate by the action of hydrosulphuric acid upon bismuthic salts. Bismuthic sulphide is not soluble in diluted sulphuric or hydrochloric acid, but dissolves easily in nitric acid. *Bolivite* is an oxysulphide, $Bi_2S_3.Bi_2O_3$.

ANTIMONY.

$Sb''' = 120$ parts by weight.

243. Antimony is nearly allied to bismuth in its physical and chemical characters. It is even harder and more brittle than that metal, being easily reduced to powder. Its highly crystalline structure is another very well marked feature, and is at once perceived upon the surface of an ingot of antimony, where it is exhibited in beautiful fern-like markings (*star antimony*). Its crystals belong to the same system (the rhombohedral) as those of bismuth and arsenic. It is much lighter than bismuth (sp. gr. 6.715), and requires a higher temperature (426° C.) to fuse it, though it is more easily converted into vapour, so that, when

strongly heated in air, it emits a thick white smoke, the vapour being oxidised. Like bismuth, it is but little affected by hydrochloric or dilute sulphuric acid, but nitric acid oxidises it, though it dissolves very little of the metal, the greater part being left in the form of antimonic acid. The best mode of dissolving antimony is to boil it with hydrochloric acid and to add nitric acid by degrees. Antimony decomposes steam at a red heat.

Antimony is chiefly found in nature as *grey antimony ore*, *stibnite*, which is a sulphide of antimony (Sb_2S_3), occurring in Cornwall, but much more abundantly in Hungary. It is found in veins associated with galena, iron pyrites, quartz, and heavy spar. In order to purify it from these, advantage is taken of its easy fusibility, the ore being heated upon the hearth of a reverberatory furnace, with some charcoal to prevent oxidation, when the sulphide of antimony melts and collects below the impurities, whence it is run off and cast into moulds. The product thus obtained is known in commerce as *crude antimony*, and contains sulphides of arsenic, iron, and lead.

To obtain *regulus of antimony*, or metallic antimony, the sulphide of antimony is sometimes fused in contact with refuse metallic iron (such as the clippings of tin-plate), when sulphide of iron is formed, and collects as a fused slag upon the surface of the melted antimony; $Sb_2S_3 + Fe_3 = 3FeS + Sb_2$. The antimony thus obtained always contains a considerable proportion of iron.

A purer product is procured by another process, which consists in roasting the sulphide in a reverberatory furnace at a temperature insufficient to fuse it, for about twelve hours, when most of the sulphur and arsenic are expelled as sulphurous and arsenious oxides, carrying with them a considerable quantity of oxide of antimony. The roasted ore has a brown-red colour, and contains both oxide and sulphide of antimony: it is mixed into a paste with $\frac{1}{5}$th its weight of charcoal saturated with a strong solution of sodium carbonate. The mixture is strongly heated in crucibles, when the oxide of antimony is reduced by the charcoal, and a portion of the sulphide, having been converted into oxide by double decomposition with the sodium carbonate—

$$Sb_2S_3 + 3Na_2CO_3 = Sb_2O_3 + 3Na_2S + 3CO_2$$

—is also reduced, the remainder of the sulphide combining with the sodium sulphide to form a slag which floats above the metallic antimony; the latter is cast into ingots for the market, and the slag, known as *crocus of antimony* (chiefly $3Na_2S.Sb_2S_3$), is employed for the preparation of some of the compounds of the metal.

On the small scale, antimony may be extracted from the sulphide by fusing it in an earthen crucible with 4 parts of commercial potassium cyanide, at a moderate heat; or by mixing 4 parts of the sulphide with 3 of bitartrate of potash and 1½ of nitre, and throwing the mixture, by small portions, into a red-hot crucible, when the sulphur is oxidised, and converted into potassium sulphate, by the nitre, which is not present in sufficient quantity to oxidise the antimony, so that the metal collects at the bottom of the crucible.

When tartar-emetic is strongly heated in a closed crucible, an alloy of antimony and potassium is obtained which decomposes water rapidly and becomes hot when exposed to air.

The brittleness of antimony renders it useless in the metallic state except for the construction of thermo-electric piles, where it is in conjunction with bismuth. Antimony is employed, however, to harden several useful alloys, such as type-metal, shrapnel-shell bullets, Britannia metal, and pewter.

Amorphous antimony.—The ordinary crystalline form of antimony may be obtained, like copper and other metals, by decomposing solutions containing the metal by transmitting the galvanic current (the solution should not contain more than 7 per cent. of antimonious chloride); but in some cases the antimony is deposited from very strong solutions in an amorphous condition, having properties very different from those of ordinary antimony. The best mode of obtaining it in this form is to decompose a solution of 1 part of tartar emetic (tartrate of antimony and potassium) in 4 parts of a strong solution of antimony trichloride (obtained by heating hydrochloric acid with antimony sulphide till it refuses to dissolve any more), by the aid of three cells of Smee's battery, the zinc of which is connected by a copper wire with a plate of copper immersed in the antimonial solution, whilst the platinised silver of the battery is connected with a plate of antimony in the same solution, at some little distance from the copper plate. The deposit of antimony which forms upon the copper has a brilliant metallic appearance, but is amorphous, and not crystalline, like the ordinary metal. If it be gently heated or sharply struck, its temperature rises suddenly to about 200° C., and it becomes converted into a form more nearly resembling crystalline antimony. At the same time, however, thick fumes of antimony trichloride are evolved, for this substance is always present in the amorphous antimony to the amount of 5 or 6 per cent.,* so that, as yet, there is not sufficient evidence to establish beyond a doubt the existence of a pure amorphous form of antimony corresponding to amorphous phosphorus, however probable this may appear from the chemical resemblance between these elements.

244. OXIDES OF ANTIMONY, Sb_2O_3, Sb_2O_4, Sb_2O_5.—*Trioxide* or *sesquioxide of antimony*, or *antimonious oxide*, Sb_2O_3, is formed when antimony burns in air (*flowers of antimony*), and is prepared on a large scale by roasting either the metal or the sulphide in air, for use in painting as a substitute for white lead. It is also found in nature as *white antimony ore*, or *valentinite*. Antimonious oxide forms a crystalline powder, usually composed of minute prisms having the shape of the rarer form of arsenious oxide (page 246), whilst occasionally it is obtained in crystals similar to those of the common octahedral arsenious oxide, with which, therefore, antimonious oxide is *isodimorphous*. The octahedral form appears to be produced only when the prismatic form is slowly sublimed in a non-oxidising atmosphere. The mineral *exitéle* is prismatic oxide of antimony, and *senarmontite* is the octahedral form of that oxide. When heated in air the oxide assumes a yellow colour, afterwards takes fire, smoulders, and becomes converted into the antimonious antimoniate ($Sb_2O_3.Sb_2O_5 = Sb_2O_4$), which was formerly regarded as an independent oxide. Sb_2O_3 may be obtained by oxidising antimony with very weak nitric acid, or better, by dissolving antimony sulphide in strong HCl, boiling off all H_2S, diluting largely with water, washing the precipitated oxychloride by decantation till it is no longer acid, and boiling it with a strong solution of sodium carbonate; $2SbOCl + Na_2CO_3 = Sb_2O_3 + 2NaCl + CO_2$. The sesquioxide is insoluble in water, but acids dissolve it, forming salts, though its basic properties are weak, and its salts rather ill defined. A hot solution of hydropotassium tartrate, $HKC_4H_4O_6$, dissolves it, forming *tartar-emetic*, $SbO.KC_4H_4O_6$. Potash and soda are also capable of dissolving it, whence it is sometimes called *antimonious anhydride*, corresponding to nitrous anhydride. Two crystallised *antimonites of sodium* have been ob-

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* It has been plausibly suggested that the sudden rise of temperature may be due to the presence of an antimony compound analogous to the so-called chloride of nitrogen, the latter element being connected with antimony by several chemical analogies.

tained, the neutral antimonite $NaSbO_2.6Aq$, and the triantimonite $NaSbO_2.Sb_2O_3.Aq$; the former is sparingly soluble, the latter almost insoluble in water.

The specific gravity of the vapour of Sb_2O_3 is 288 ($H = 1$). Hence the molecule or two volumes of vapour would weigh 576, and would be expressed by $(Sb_2O_3)_2$. The same holds good for As_2O_3 (see p. 237).

Antimony tetroxide, Sb_2O_4, is important because it is the product of the action of heat upon either of the other oxides in contact with air, so that antimony is often weighed in this form in quantitative analysis. It is readily obtained by boiling antimony with nitric acid, evaporating to dryness, and heating the residue to redness. It is yellow while hot, and becomes white on cooling.

Antimony ash, obtained by roasting the grey sulphide in air, consists chiefly of Sb_2O_4, and is used for preparing other antimony compounds.

Thus, tartar-emetic may be obtained by boiling Sb_2O_4 with hydropotassium tartrate; $Sb_2O_4 + HKC_4H_4O_6 = SbKC_4H_4O_7$ (tartar-emetic) + $SbHO_3$ (metantimonic acid). This leads to the belief that Sb_2O_4 really contains the two groups $Sb'''O_2$ and $Sb^{V}O_2$, of which the first gives rise to tartar-emetic, and the second to metantimonic acid. For $Sb'''O_2 + HKC_4H_4O_6 = Sb'''KC_4H_4O_7 + HO$, and $Sb^{V}O_2 + HO = Sb^{V}HO_3$.

The presence of Sb_2O_4 in Sb_2O_3 can be detected by dissolving in HCl and adding KI, when iodine will be liberated—

$$Sb_2O_4 + 2KI + 8HCl = 2SbCl_3 + 2KCl + 4H_2O + I_2.$$

Antimonic oxide, Sb_2O_5, is formed when antimony is oxidised by nitric acid; it is a white powder, which should be well washed and dried at 280° C.

It will be remembered that As_2O_5 may be obtained in a similar way, but not P_2O_5. Sb_2O_5 is a pale yellow amorphous powder, insoluble in water, and decomposed at 300° C., leaving Sb_2O_4. It is dissolved by potash, forming the antimonate.

Antimonious acid, $HSbO_2$, corresponding to nitrous acid, is said to have been obtained as $2HSbO_2.3Aq$, in the form of a white precipitate, by decomposing sodium antimonite with nitric acid.

Antimonic acid, $HSbO_3$, corresponding to nitric acid, is precipitated as $HSbO_3.2Aq$ by adding nitric acid to solution of potassium antimonate. It is a white powder, slightly soluble in water, and easily so in potash.

Potassium antimonate, $KSbO_3$, is made by gradually adding 1 part of powdered antimony to 4 parts of nitre fused in a clay crucible. The mass is powdered and washed with warm water to remove the excess of nitre and the potassium nitrite, when the anhydrous potassium antimoniate is left; and on boiling this for an hour or two with water, it becomes hydrated, and dissolves. The solution, when evaporated, leaves a gummy mass of *potassium antimonate*, having the composition $2KSbO_3.5Aq$. This dissolves in warm water, and is decomposed by boiling for some time, yielding an acid antimonate $K_4H_2(SbO_3)_6.9Aq$.

Sodium antimonate, $2NaSbO_3.7Aq$, is prepared like the potassium salt.

Ammonium antimonate, NH_4SbO_3, is obtained as a crystalline powder, insoluble in water, by dissolving $HSbO_3$ in warm ammonia.

A *basic lead antimonate* is used in oil-painting as *Naples yellow*.

Metantimonic acid, $H_4Sb_2O_7$, should really be called pyro-antimonic acid, since it corresponds to pyrophosphoric acid, $H_4P_2O_7$. It is obtained as a white precipitate by decomposing antimonic chloride with water; $2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl$. It is rather more soluble in water than antimonic acid, and dissolves in cold ammonia. When heated to 200° C., it is converted into antimonic acid; $H_4Sb_2O_7 = 2HSbO_3 + H_2O$. This resembles the conversion of pyrophosphoric into metaphosphoric acid by the action of heat.

Potassium metantimonate, $K_4Sb_2O_7$, is made by fusing the antimonate with potash, in a silver crucible; $2KSbO_3 + 2KHO = K_4Sb_2O_7 + H_2O$. On dissolving in water and evaporating, crystals of the metantimonate are obtained, but water decomposes these into potash and *potassium dimetantimonate*, $K_2H_2Sb_2O_7$, which forms a crystalline powder containing 6Aq. It is sparingly soluble in cold water, but dissolves in warm water. The solution forms a valuable test for sodium, which it precipitates in the form of $Na_2H_2Sb_2O_7.6Aq$. When long kept, the solution of potassium dimetantimonate becomes converted into antimonate, which does not precipitate sodium; $K_4Sb_2O_7 + H_2O = 2KSbO_3 + 2KHO$. Acids precipitate metantimonic acid, which dissolves in HCl. Nearly all metallic solutions yield precipitates with the potassium dimetantimonate, so that all other metals must be removed from the solution before testing for sodium.

245. *Antimonetted hydrogen*, or *hydric antimonide*, SbH_3, is not known in the pure state, but is obtained, mixed with H, when an alloy of antimony with zinc is acted on by dilute sulphuric acid, or when a solution of an antimony salt, tartar-emetic, for example, is poured into a hydrogen apparatus containing zinc and dilute sulphuric acid (see page 242). Its production forms the most delicate test for antimony, as in the parallel case of arsenic, but the one cannot be mistaken for the other, if the following differences be observed. The SbH_3 burns with a *greenish* flame, which deposits a *soot-black* spot upon a porcelain crucible lid (fig. 220). This spot dissolves when a drop of yellow ammonium sulphide is placed on it with a glass rod, and, on evaporation, gives an orange film of Sb_2S_3. When the tube through which the gas passes is heated (fig. 221), metallic antimony is deposited at the heated part, and not beyond it, like arsenic. When the gas is passed into silver nitrate, the antimony is precipitated as black silver antimonide; $SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$ (whereas arsenic passes into solution as arsenious acid), and gives a black precipitate of metallic silver.

Sulphur decomposes SbH_3 in sunlight or at 100° C., but not in the dark; $2SbH_3 + 3S_2 = Sb_2S_3 + 3H_2S$. The reactions with silver nitrate and with sulphur prove the composition of the gas to be SbH_3, so that it is analogous to AsH_3, PH_3, and NH_3.

If the hydrogen antimonide be prepared by the action of dilute sulphuric acid upon an alloy of 2 parts of antimony with 3 parts of zinc, and the first portions collected separately and cooled to −91° C., it solidifies, but on raising the temperature to about −60° it is decomposed, antimony being deposited. This explains why so little of the compound is obtained in the gas made under ordinary conditions.

246. CHLORIDES OF ANTIMONY.—Chlorine and antimony combine readily with evolution of heat and light; the chlorides are among the most important compounds of this metal.

Trichloride of antimony, or *antimonious chloride*, $SbCl_3$ (= 2 vols.), may be prepared by distilling three parts of powdered antimony with eight parts of corrosive sublimate, when calomel and an amalgam of antimony are left, and the trichloride of antimony distils over; $Sb_2 + 2HgCl_2 = SbCl_3 + SbHg + HgCl$. It can also be obtained by boiling powdered antimony or sulphide of antimony to dryness with strong sulphuric acid, and distilling the antimonious sulphate thus obtained with common salt. The trichloride is a soft crystalline fusible solid, whence its old name of *butter of antimony*. It fuses at 72° C. and boils at 223° C. It may be dissolved in a small quantity of water, but a large quantity of water decomposes it, forming a bulky white precipitate, which is an *oxychloride of antimony*; $SbCl_3 + H_2O = 2HCl + SbOCl$; this is a decomposition similar to that which occurs with PCl_3, $AsCl_3$, and $BiCl_3$. By long washing, $2SbOCl + H_2O = 2HCl + Sb_2O_3$. When hot water is added to a hot solution of trichloride of antimony in hydrochloric acid, minute prismatic needles are deposited, containing $Sb_4Cl_2O_5$, and formerly called *powder of Algaroth*. The same body is formed when SbOCl is heated; $5SbOCl = SbCl_3 + Sb_4Cl_2O_5$. Trichloride of antimony is occasionally used in surgery as a caustic; it also serves as a bronze for gun-barrels, upon which it deposits a film of antimony.

Pentachloride of antimony, or *antimonic chloride* ($SbCl_5$), is prepared by heating coarsely powdered antimony in a retort, through which a stream of dry chlorine is passed (fig. 205), the neck of the retort being fitted into an adapter, which serves to condense the pentachloride. One ounce of antimony will require the chlorine from about 6 oz. of common manganese and 18 oz. (measured) of hydrochloric acid. The pure pentachloride is a colourless fuming liquid of a very suffocating odour; it combines energetically with a small quantity of water, forming a crystalline hydrate, $SbCl_5.4Aq$, but an excess of water decomposes it into hydrochloric and metantimonic acids, the latter forming a white precipitate; $2SbCl_5 + 7H_2O = 10HCl + H_4Sb_2O_7$. If it be dropped into water kept cool by ice, it yields *antimony oxytrichloride* as a deliquescent crystalline body; $SbCl_5 + H_2O = SbOCl_3 + 2HCl$. Pentachloride of antimony is employed by the chemist as a chlorinating agent; thus, olefiant gas (C_2H_4), when passed through it, is converted into Dutch liquid ($C_2H_4Cl_2$), and carbonic oxide into phosgene gas, the pentachloride of antimony being converted into trichloride. $SbCl_5$ is partially decomposed by distillation into $SbCl_3$ and Cl_2.

The pentachloride of antimony is the analogue of pentachloride of phosphorus, and a *chlorosulphide of antimony* ($SbCl_3S$), corresponding to chlorosulphide of phosphorus, is obtained as a white crystalline solid by the action of hydrosulphuric acid upon pentachloride of antimony.

247. SULPHIDES OF ANTIMONY.—*Antimonious sulphide*, or *sesquisulphide of antimony* (Sb_2S_3), has been noticed as the chief ore of antimony. It is abundant in Borneo. It is a heavy mineral (sp. gr. 4.63), of a dark grey colour and metallic lustre, occurring in masses which are made up of long prismatic needles. It fuses easily, and may be sublimed unchanged out of contact with air. It is easily recognised by heating it, in powder, with hydrochloric acid, when it evolves the odour of hydrosulphuric acid, and if the solution be poured into water, it deposits an orange precipitate (page 195). This orange sulphide, which is a compound of Sb_2S_3 with water, is also obtained by adding hydrosulphuric acid to a solution of a salt of antimony (for example, tartar-emetic) acidulated with hydrochloric acid. It may be converted into the grey

sulphide at 200° C. The orange variety constitutes the *antimony vermilion*, the preparation of which has been described at page 212. Native sulphide of antimony is employed, in conjunction with potassium chlorate, in the *friction-tube* for firing cannon; it is also used in *percussion caps*, together with potassium chlorate and mercuric fulminate. Its property of deflagrating with a bluish-white flame when heated with nitre, renders it useful in compositions for coloured fires.

Glass of antimony is a transparent red mass obtained by roasting antimonious sulphide in air, and fusing the product; it contains about 8 parts of oxide and 1 part of sulphide of antimony. It is used for colouring glass yellow.

Red antimony ore is an oxysulphide of antimony, $Sb_2O_3.2Sb_2S_3$.

Antimonic sulphide (Sb_2S_5) is obtained as a bright orange-red precipitate by the action of hydrosulphuric acid upon a solution of pentachloride of antimony in hydrochloric acid. It is decomposed by heat into Sb_2S_3 and S_2. When boiled with hydrochloric acid, $Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2$, showing the trivalence of antimony to be stronger than the quinquivalence.

Both the sulphides of antimony are capable of combining with the alkaline sulphides to form *sulphantimonites* and *sulphantimonates* respectively. Hence they are easily dissolved by alkalies and alkaline sulphides; for example, $Sb_2S_3 + 6KHO = K_3SbO_3$ (*antimonite*) + K_3SbS_3 (*sulphantimonite*) + $3H_2O$. Hydrochloric acid reprecipitates all the antimony as Sb_2S_3. Even metallic antimony, in powder, is dissolved when gently heated with solution of potassium sulphide in which sulphur has been dissolved, any lead or iron which may be present being left in the residue, so that the antimony may be tested by this process as to its freedom from those metals.

Mineral kermes is a variable mixture of oxide and sulphide of antimony, which is deposited as a reddish-brown powder from the solution obtained by boiling sulphide of antimony with potash or soda. It was formerly much valued for medicinal purposes. *Kermes* was the Arabic name of an insect formerly used in dyeing scarlet.

Schlippe's salt is the sodium sulphantimonate ($Na_3SbS_4.9H_2O$), and may be obtained in fine transparent tetrahedral crystals by dissolving Sb_2S_3 in NaHO and adding sulphur. This salt is sometimes used in photography.

Potassium sulphantimonate. $K_3SbS_4.9Aq$, has been obtained.

Antimonious sulphate, $Sb_2(SO_4)_3$, is formed when antimony is boiled with strong H_2SO_4. It crystallises in needles, which are decomposed by water into a soluble acid sulphate and an insoluble basic sulphate.

Antimony phosphide, SbP, has been obtained by mixing solutions of antimonious bromide and phosphorus in carbon disulphide. It forms an insoluble red powder.

TIN.

$Sn = 118$ parts by weight.

248. Tin is by no means so widely diffused as most of the other metals which are largely used, and is scarcely ever found in the metallic state in nature. Its only important ore is that known as *tin-stone*, which is a binoxide of tin, SnO_2, and is generally found in veins traversing quartz,

granite, or slate. It is generally associated with arsenical iron pyrites, and with a mineral called *wolfram*, which is a tungstate of iron and manganese.

Tin-stone is sometimes found in alluvial soils in the form of detached rounded masses; it is then called *stream tin ore*, and is much purer than that found in veins, for it has undergone a natural process of oxidation and levigation exactly similar to the artificial treatment of the impure ore. These detached masses of stream tin ore are not unfrequently rectangular prisms with pyramidal terminations.

The Cornish mines furnish the largest supplies of tin, and those of Malacca and Banca stand next. Tin-stone is also found in Bohemia, Saxony, California, and Australia. At the Cornish tin-works the purer portions of the ore are picked out by hand, and the residue, which contains quartz and other earthy impurities, together with copper pyrites and arsenical iron pyrites, is reduced to a coarse powder in the stamping-mills, and washed in a stream of water. The tin-stone, being extremely hard, is not reduced to so fine a powder as the pyritous minerals associated with it, and these latter are therefore more readily carried away by the stream of water than the tin-stone. The removal of the foreign matters from the ore is also much favoured by the high specific gravity of the binoxide of tin, which is 6.5, whilst that of sand or quartz is only 2.7, so that the latter would be carried off by a stream which would not disturb the former. So easily and completely can this separation be effected, that a sand containing less than 1 per cent. of tin-stone is found capable of being economically treated.

In order to expel any arsenic and sulphur which may still remain in the washed ore, it is roasted in quantities of 8 or 10 cwts. in a reverberatory furnace, when the sulphur is disengaged in the form of sulphurous acid gas, and the arsenic in that of arsenious oxide, the iron being left in the state of ferric oxide, and the copper partly as sulphate of copper, partly as unaltered sulphide. To complete the oxidation of the insoluble sulphide of copper, and its conversion into the soluble sulphate, the roasted ore is moistened with water and exposed to the air for some days, after which the whole of the copper may be removed by again washing with water.

A second washing in a stream of water also removes the ferric oxide in a state of suspension, and this is much more easily effected than when the iron was in the form of pyrites, since the difference between the specific gravity of this mineral (5.0) and that of the tin-stone (6.5) is far less than that between ferric oxide and tin-stone.

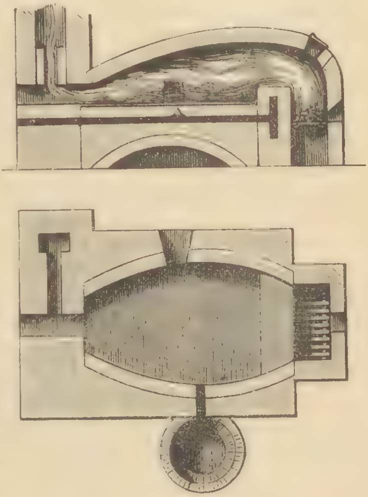

Fig. 246.

The ore thus purified contains between 60 and 70 per cent. of tin;

it is mixed very intimately with about $\frac{1}{8}$th of powdered coal, and a little lime or fluor spar to form a fusible slag with the earthy impurities; the mixture is sprinkled with water to prevent its dispersion by the draught of air, and thrown on the hearth (A, fig. 246) of a reverberatory furnace, in charges of between 20 and 25 cwts.

The temperature is not permitted to rise too high at first, lest a portion of the oxide of tin should combine with the silica to form a silicate, from which the metal would be reduced with difficulty.

During the first six or eight hours the doors of the furnace are kept shut, so as to exclude the air and favour the reducing action of the carbon upon the binoxide of tin, the oxygen of which it converts into carbonic oxide, leaving the tin in the metallic state to accumulate upon the hearth beneath the layer of slag. When the reduction is deemed complete, the mass is well stirred with an iron paddle to separate the metal from the slag; the latter is run out first, and the tin is then drawn off into an iron pan (B), where it is allowed to remain at rest for the dross to rise to the surface, and is ladled out into ingot moulds.

The slags drawn out of the smelting-furnace are carefully sorted, those which contain much oxide of tin being worked up with the next charge of ore, whilst those in which globules of metallic tin are disseminated are crushed, so that the metal may be separated by washing in a stream of water.

The tin, when first extracted from the ore, is far from pure, being contaminated with small quantities of iron, arsenic, copper, and tungsten. In order to purify it from these, the ingots are piled into a hollow heap near the fire-bridge of a reverberatory furnace, and gradually heated to the fusing point, when the greater portion of the tin flows into an outer basin, whilst the remainder is converted into the binoxide, which remains as dross upon the hearth, together with the oxides of iron, copper, and tungsten, the arsenic having passed off in the form of arsenious oxide. Fresh ingots of tin are introduced at intervals, until about 5 tons of the metal have collected in the basin, which is commonly the case in about an hour after the commencement of the operation.

The specific gravity of tin being very low (7.285), any dross which may still remain mingled with it does not separate very readily; to obviate this, the molten metal is well agitated by stirring with wet wooden poles, or by lowering billets of wet wood into it, when the evolved bubbles of steam carry the impurities up to the surface in a kind of froth; the stirring is continued for about three hours, and the metal is allowed to remain at rest for two hours, when it is skimmed and ladled into ingot moulds. It is found that, in consequence of the lightness of the metal, and its tendency to separate from the other metals with which it is contaminated, the ingots which are cast from the metal first ladled out of the pot are purer than those from the bottom; this is shown by striking the hot ingots with a hammer, when they break up into the irregular prismatic fragments known as *dropped* or *grain-tin*, the impure metal not exhibiting this extreme brittleness at a high temperature. The tin imported from Banca is celebrated for its purity (*Straits tin*).

When the tin ore contains wolfram, $[FeMn]WO_4$, which has sp. gr. 7.3, it remains behind with the prepared tin ore, and must be removed before smelting, by fusion with sodium carbonate in a reverberatory furnace, when the tungstic acid is converted into sodium tungstate, which is dissolved out by water and crystallised. This salt finds an application in calico-printing.

On the small scale, tin may be extracted from tin-stone by fusing 100 grains with 20 grains of dried sodium carbonate, and 20 of dried borax, in a crucible lined with charcoal, exactly as in the extraction of iron (see p. 330).

The extraction is more easily effected by fusing 100 grains of tin-stone with 500 grains of potassium cyanide for fifteen minutes at a red heat.

249. PROPERTIES OF TIN.—Tin is remarkable for its lustre and whiteness, in which it rivals silver, but is at once distinguished from it by its greater fusibility, and by its oxidising when heated in air. It is the most fusible of the metals in common use (228° C.), much lighter than silver, sp. gr. 7.28, and emits a curious grating sound when bent; it is harder than lead, but softer than zinc; very malleable at ordinary temperatures (*tin-foil*), brittle at 200° C. (*dropped* or *grain tin*); not vaporised except at very high temperatures. It has the lowest tenacity of all the metals in common use, and, therefore, its ductility is very low, only one other common metal, lead, being more difficult to draw into wire at the common temperature. Tin may, however, be drawn at 100° C. Only gold, silver, and copper surpass it in malleability.

Tin decomposes steam at a red heat. It is scarcely affected by air or water at common temperatures, and is therefore used for tinning other metals. Tin is easily soluble in strong hydrochloric acid, which distinguishes it from silver, and it is converted into a white nearly insoluble powder by nitric acid, which distinguishes it from all other metals except antimony.

Tin-foil is made from bars of the best tin, which are hammered down to a certain thinness, then cut up, laid upon each other, and again beaten till extended to the required degree.

Tin-plate is made by coating sheets of iron with a layer of tin; the best kind, known as *block tin*, being that which is covered with the thickest layer of tin, and afterwards hammered upon a polished anvil in order to consolidate the coating and make it adhere more firmly. Tin, being unaltered by exposure to air at the ordinary temperature, will effectually protect the iron from rust as long as the coating of tin is perfect, but as soon as a portion of the tin is removed so as to leave the iron exposed, corrosion will take place very rapidly, because the two metals form a galvanic couple, which will decompose the water (charged with carbonic acid) deposited upon them from the air, and the iron, having the greater attraction for oxygen, will be the metal attacked. In the case of galvanised iron (coated with zinc), on the contrary, the zinc would be the metal attacked, and hence the greater durability of this material under certain conditions.

For the manufacture of the best tin-plate, the very best iron refined with charcoal (see page 318) is employed, and the most important part of the process consists in cleansing the iron plates from every trace of oxide which would prevent the adhesion of the tin. To effect this they are made to undergo several processes, of which the most important are—(1) immersion in diluted sulphuric acid; (2) heating to redness;

(3) hammering and rolling to scale off the oxide; (4) steeping in sour bran; (5) immersion in mixed diluted sulphuric and hydrochloric acids; (6) scouring with bran; (7) washing with water; they are then dried for an hour in a vessel of melted tallow, which prevents contact of air, and immersed for an hour and a half in melted tin, the surface of which is protected from oxidation by tallow; after draining, they are dipped a second time into the tin to thicken the layer; then transferred to a bath of hot tallow to allow the superfluous tin to run down to the lower edge, whence it is afterwards removed by liquefying it in a vessel of melted tin, and shaking it off by a sharp blow. About 8 lbs. of tin are required to cover 225 plates, weighing 112 lbs.

To recover the tin from tin-plate cuttings they are boiled with caustic soda and litharge; $Sn + 2NaOH + 2PbO = Na_2SnO_3 + Pb_2 + H_2O$. The sodium stannate, Na_2SnO_3, is used in dye-works, and the precipitated lead is again converted into litharge by heating in air.

Terne-plate is iron coated with an alloy of tin and lead.

In tinning the interior of copper vessels, in order to prevent the contamination of food with the copper, the surface is first thoroughly cleaned from oxide by heating it and rubbing over it a little sal-ammoniac, which decomposes any oxide of copper, converting it into the volatile chloride of copper ($CuO + 2NH_4Cl = CuCl_2 + H_2O + 2NH_3$). A little resin is then sprinkled upon the metallic surface, to protect it from oxidation, and the melted tin is spread over it with tow.

Pins (made of brass wire) are coated with tin by boiling them with cream of tartar (bitartrate of potash), common salt, alum, granulated tin, and water; the tin is dissolved by the acid liquid, from which solution it is reduced by electrolytic action, for the tin is more highly electro-positive than the brass, and the latter acts as the negative plate.

250. ALLOYS OF TIN.—Tin is the chief metal used for making white alloys, some of which resemble silver in appearance. *Britannia metal* consists chiefly of tin (about 80 per cent.) hardened by antimony (about 10 per cent.) and a little copper. Base silver coin consists chiefly of tin. Pewter consists of 4 parts of tin and 1 part of lead. Much inferior tin foil is made of pewter. The fusibility of tin recommends it for solder. The solder employed for tin wares is an alloy of tin and lead in various proportions, sometimes containing 2 parts of tin to 1 of lead (fine solder), sometimes equal weights of the two metals (common solder), and sometimes 2 parts of lead to 1 of tin (coarse solder). All these alloys melt at a lower temperature than tin, and, therefore, than lead. In applying solder, it is essential that the surfaces to be united be quite free from oxide, which would prevent adhesion of the solder; this is insured by the application of sal-ammoniac, or of hydrochloric acid,* or sometimes of powdered borax, remarkable for its ready fusibility and its solvent power for the metallic oxides.

Gun metal is an alloy of 90.5 parts of copper with 9.5 of tin, especially valuable for its tenacity, hardness, and fusibility. In preparing this alloy, it is usual to melt the tin, in the first place, with twice its weight of copper, when a white, hard, and extremely brittle alloy (*hard metal*) is obtained. The remainder of the copper is fused in a de-oxidising flame on the hearth of a reverberatory furnace, and the hard metal thoroughly mixed with it, long wooden stirrers being employed. A quantity of old gun metal is usually melted with the copper, and facilitates the mixing of the metals. When the metals are thoroughly mixed, the oxide is removed from the surface, and the gun metal is run into moulds made of loam, the stirring being continued during the running, in order to prevent the separation, to which this alloy is very liable, of a white alloy containing a larger proportion of tin, which has a lower specific gravity, and would chiefly collect in the upper part of the casting (forming *tin-spots*). In casting cannon (erroneously called *brass* guns) the mould is placed perpendicularly, with the muzzle upwards, the upper part of the mould being about 3 feet longer than is required for the gun, so that a superfluous cylinder of metal or *dead-head* is formed, in which the separated alloy collects, together with any oxide or dross which may have run out with the metal; this dead-head is cut off before the gun is turned and bored. The metal is run into the mould at a temperature as near its point of solidification as possible, so as to diminish the chance of separation. The purest commercial qualities of copper and tin are always employed in gun metal.

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* It is customary to *kill* the hydrochloric acid by dissolving some zinc in it. The chloride of zinc is probably useful in protecting the work from oxidation.

The brittle white alloy alluded to above as *hard metal* appears to be a chemical compound having the formula $SnCu_4$ (which requires 31.8 per cent. of tin and 68.2 per cent. of copper), though the alloy which has the highest density, and which bears repeated fusion without alteration in its composition, corresponds to the formula $SnCu_3$ (38.2 per cent. of tin). It is probably one of these alloys which forms the tin-spots or flaws in gun-metal castings.

Bronze is essentially an alloy of copper and tin, containing more tin than gun metal; its composition is varied according to its application, small quantities of zinc and lead being often added to it. Bronze is affected by changes of temperature, in a manner precisely the reverse of that in which steel is influenced, for it becomes hard and brittle when allowed to cool slowly, but soft and malleable when quickly cooled. The art of making bronze was practised before any progress had been made in working iron, and ancient weapons were very commonly of this material. *Bronze coin* (substituted for the copper coinage) is composed of 95 copper, 4 tin, and 1 zinc.

Manganese-bronze, an alloy of ordinary bronze with manganese, is said to rival bar-iron in tenacity and extensibility.

Bell metal is an alloy of about 4 parts of copper and 1 of tin, to which lead and zinc are sometimes added. The metal of which musical instruments are made generally contains the same proportions of copper and tin as bell metal. At a little below a dark red heat, this alloy may be hammered into thin plates, by which Riche and Champion have succeeded in imitating the celebrated Chinese gongs.

Speculum metal, employed for reflectors in optical instruments, consists of 2 parts of copper and 1 of tin, to which a little zinc, arsenic, and silver are sometimes added to harden it and render it susceptible of a high polish.

A superior kind of *type metal* is composed of 1 part of tin, 1 of antimony, and 2 of lead.

Tin is not dissolved by nitric acid, but is converted into a white powder, *metastannic acid;* hydrochloric acid dissolves it with the aid of heat, evolving hydrogen; but the best solvent for tin is a mixture of hydrochloric with a little nitric acid. When the metal is acted upon by hydrochloric acid, it assumes a crystalline appearance, which has been turned to account for ornamenting tin-plate. If a piece of common tin-plate be rubbed over with tow dipped in a warm mixture of hydrochloric and nitric acids, its surface is very prettily diversified (*moiré métallique*); it is usual to cover the surface with a coloured transparent varnish.

A mixture of 1 vol. H_2SO_4, 2 vols. HNO_3, and 3 vols. water dissolves tin in the cold, evolving nearly pure nitrous oxide. The solution is precipitated when heated. Poured into boiling water, all the tin is thrown down as metastannic acid.

Commercial tin is liable to contain minute quantities of lead, iron, copper, arsenic, antimony, bismuth, gold, molybdenum, and tungsten. Pure tin may be precipitated in crystals by the feeble galvanic current excited by immersing a plate of tin in a strong solution of stannous chloride, covered with a layer of water, so that the metal may be in contact with both layers of liquid.

251. OXIDES OF TIN.—Two oxides of this metal are known—stannous oxide, SnO, and stannic oxide, SnO_2.

Protoxide of tin (SnO), or *stannous oxide*, is a substance of little practical importance, obtained by heating stannous oxalate out of contact with air: $SnC_2O_4 = SnO + CO_2 + CO$. It is a black powder which burns when heated in air, becoming SnO_2. It is a feebly basic oxide, and therefore dissolves in the acids; it may also be dissolved by a strong solution of potash, but is then easily decomposed into metallic tin and stannic oxide which combines with the potash.

Binoxide of tin (SnO_2), or *stannic oxide*, has been mentioned as the chief ore of tin, and is formed when tin is heated in air. *Tin-stone*, or *cassiterite*, as the natural form of this oxide is called, occurs in very hard square prisms, usually coloured brown by ferric oxide. In its insolubility in acids it resembles crystallised silica, and, like that substance, it forms, when fused with alkalies or their carbonates, compounds which are soluble in water; these compounds are termed *stannates*, the binoxide of tin being known as *stannic anhydride*. The artificial SnO_2 dissolves in hot strong sulphuric acid, and is precipitated on adding water. It is easily reduced when heated in hydrogen, and is converted into $SnCl_4$ when heated in HCl gas.

Sodium stannate is prepared, on the large scale, for use as a mordant by calico-printers. The prepared tin ore (page 359) is heated with solution of sodium hydrate, and boiled down till the temperature rises to 500° or 600° F.; or the tin ore is fused with sodium nitrate, when the nitric acid is expelled. It crystallises easily in hexagonal tables having the composition $Na_2SnO_3.4Aq$, which dissolve easily in cold water, and are partly deposited again when the solution is heated. Prismatic crystals have been obtained of $Na_2SnO_3.10Aq$, like $Na_2CO_3.10Aq$. Most normal salts of the alkalies also cause a separation of sodium stannate from its aqueous solution. The solution of sodium stannate has, like the silicate, a strong alkaline reaction, and when neutralised by an acid, yields a precipitate of stannic acid, H_2SnO_3, or $SnO(HO)_2$. If the solution of sodium stannate be added to an excess of hydrochloric acid, the stannic acid remains in solution, and if the liquid be dialysed (see page 114), a jelly is first formed, which gradually liquefies as the sodium chloride diffuses away, and eventually a pure aqueous solution of stannic acid is obtained, which is very easily gelatinised by the addition of a minute quantity of hydrochloric acid, or of some neutral salt. The great similarity between stannic and silicic acids is here very remarkable. When heated, stannic acid is converted into metastannic anhydride (Sn_5O_{10}).

Metastannic acid, $H_{10}Sn_5O_{15}$ (dried at 100° C.), is obtained as a white crystalline hydrate (with 5Aq) when tin is oxidised by nitric acid; when washed with water and dried by exposure to air, it has the above composition. When heated, it assumes a yellowish colour, and a hardness resembling that of powdered tin-stone. *Putty powder*, used for polishing, consists of metastannic anhydride; as found in commerce, it generally contains much oxide of lead. Metastannic acid is insoluble in water and diluted acids, and when *fused* with hydrated alkalies, is converted into a soluble stannate; but if *boiled* with solution of potash it is dissolved in the form of potassium metastannate, which will not crystallise, like the stannate, but is obtained as a granular precipitate by dissolving potassium hydrate in its solution. This precipitate has the composition $K_2Sn_5O_{11}.4Aq$; it is very soluble in water, and is strongly alkaline. When it is heated to expel the water, it is decomposed, and the potash may be washed out with water, leaving metastannic anhydride. The *sodium metastannate*, $Na_2S_5O_{11}.4Aq$, has also been obtained as a sparingly soluble crystalline powder, by the action of cold sodium hydrate on metastannic acid. The metastannic acid may be distinguished from stannic acid by the action of stannous chloride, which converts it into the yellow metastannate of tin ($SnSn_5O_{11}.4Aq$).

Stannate of tin is obtained as a yellowish hydrate by boiling stannous chloride with ferric hydrate; $Fe_2O_3 + 2SnCl_2 = SnSnO_3 + 2FeCl_2$. It is sometimes written Sn_2O_3, and called *sesquioxide of tin.*

Stannous nitrate, $Sn(NO_3)_2$, is formed when tin is dissolved in cold very dilute nitric acid: $Sn_4 + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$. It forms a yellow solution, which absorbs oxygen and deposits SnO_2.

Stannic nitrate, $Sn(NO_3)_4$, has been crystallised from a solution of stannic acid in nitric acid.

252. CHLORIDES OF TIN.—The two chlorides of tin correspond in composition to the oxides.

Stannous chloride, or *protochloride of tin* ($SnCl_2$), is much used by dyers and calico-printers, and is prepared by dissolving tin in hydrochloric acid, when it is deposited, on cooling, in lustrous prismatic needles ($SnCl_2.2Aq$) known as *tin crystals* or *salts of tin*. *In vacuo*, over H_2SO_4, they become $SnCl_2$. The solution of the tin is generally effected in a copper vessel, in order to accelerate the action by forming a voltaic couple, of which the tin is the attacked metal. When gently heated, the crystals lose their water, and are partly decomposed, some hydrochloric acid being evolved ($SnCl_2 + H_2O = SnO + 2HCl$); but at a higher temperature, a great part of the chloride may be distilled in the anhydrous state. The crystallised stannous chloride dissolves in about one-third of its weight of water, but if much water be added, a precipitate of *stannous hydroxychloride*, $2Sn(OH)Cl.Aq$, is formed, which dissolves on adding HCl. A moderately dilute solution of stannous chloride absorbs oxygen from the air, and deposits the hydroxychloride, leaving stannic chloride in solution; $3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl$. If the solution contains much free hydrochloric acid, it remains clear, being entirely converted into stannic chloride. A strong solution of the chloride is not oxidised by the air, and the weak solution may be longer preserved in contact with metallic tin. Stannous chloride has a great attraction for chlorine as well as for oxygen, and is frequently employed as a de-oxidising or de-chlorinating agent. Tin may be precipitated from stannous chloride by the action of zinc, in the form of minute crystals. A very beautiful *tin tree* is obtained by dissolving granulated tin in strong hydrochloric acid, with the aid of heat, in the proportion of 8 measured oz. of acid to 1000 grs. of tin, diluting the solution with four times its bulk of water, and introducing a piece of zinc.

Stannous chloride is also obtained by heating tin in HCl gas, or by distilling tin with mercuric chloride; $Sn + HgCl_2 = SnCl_2 + Hg$. The mercury distils over, leaving the stannous chloride as a transparent vitreous mass which fuses at 250° C., and boils at 618° C. Above 880° C. the density of its vapour is 94.5 ($H = 1$), agreeing with the formula $SnCl_2$, but below 700° C. it is 189, corresponding to Sn_2Cl_4.

Stannic chloride, or *tetrachloride of tin* ($SnCl_4$), is obtained in solution when tin is heated with hydrochloric and nitric acids; for the use of the dyer, the solution (*nitromuriate of tin*) is generally made with chloride of ammonium (sal-ammoniac) and nitric acid. The anhydrous tetrachloride is obtained by heating tin in a current of dry chlorine, when combination takes place with combustion, and the tetrachloride distils over as a heavy (sp. gr. 2.28) colourless liquid, volatile (boiling point, 240° F., 116° C.), and giving suffocating white fumes in the air. When mixed with a little water, energetic combination takes place, and three crystalline compounds may be produced, containing three, five, and eight molecules of water. A large quantity of water causes precipitation of stannic acid. The commercial crystals are $SnCl_4.5Aq$. The anhydrous chloride is also obtained by distilling tin with an excess of mercuric chloride; $Sn + 2HgCl_2 = SnCl_4 + Hg_2$; but here, the result is opposite to that in the case of stannous chloride, as the stannic chloride distils over before the mercury. Stannic chloride forms crystallisable double salts with the alkaline chlorides. *Pink salt*, used by dyers, is a compound of stannic chloride with chloride of ammonium, $2NH_4Cl.SnCl_4$; it is colourless, but is used in dyeing red with madder. The compound $2HCl.SnCl_4.6Aq$ has been obtained in crystals.

Stannic bromide, $SnBr_4$, is crystalline, fuses at 30° C., and boils at 201° C. It dissolves in water without immediate decomposition.

253. SULPHIDES OF TIN.—The *protosulphide*, or *stannous sulphide* (SnS), may be easily prepared by heating tin with sulphur, when it forms a grey crystalline mass. It is also obtained as a dark brown precipitate by the action of hydrosulphuric acid upon a solution of stannous chloride. Stannous sulphide is not dissolved by alkalies unless some sulphur be added, which converts it into stannic sulphide. It dissolves in hot strong HCl.

Bisulphide of tin, or *stannic sulphide* (SnS_2), is commonly known as *mosaic gold* or *bronze powder*,* and is used for decorative purposes. It cannot be made by heating tin with sulphur, because it is decomposed by heat into SnS and S. It is prepared by a curious process, which was devised in 1771, and must have been the result of a number of trials. 12 parts by weight of tin are dissolved in 6 parts of mercury; the brittle amalgam thus obtained is powdered and mixed with 7 parts of sulphur and 6 of sal-ammoniac. The mixture is introduced into a Florence flask, which is gently heated in a sand-bath as long as any smell of hydrosulphuric acid is evolved; the temperature is then raised to dull redness until no more fumes are disengaged. The mosaic gold is found in beautiful yellow scales at the bottom of the flask, and sulphide of mercury and calomel are deposited in the neck. The mercury appears to be used for effecting the fine division of the tin, and the sal-ammoniac to keep down the temperature (by its volatilisation) below the point at which the stannic sulphide is converted into stannous sulphide.

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* Bronze powder is also made by powdering finely laminated alloys of copper and zinc, a little oil being used to prevent oxidation.

Mosaic gold, like gold itself, is not dissolved by hydrochloric or nitric acid, but easily by *aqua regia*. Alkalies also dissolve it when heated. On adding hydrosulphuric acid to a solution of stannic chloride, the stannic sulphide is obtained as a yellow precipitate, which is sometimes formed only on boiling. It dissolves easily in alkalies and alkaline sulphides, forming *sulphostannates*. The sodium salt, $Na_2SnS_3.2H_2O$, has been crystallised in yellow octahedra. When fused with iodine, SnS_2 forms SnS_2I_4, a fusible yellow body which does not lose iodine when heated, and dissolves in carbon disulphide, forming a brown solution which deposits red crystals like potassium dichromate; these are decomposed by boiling with water, yielding SnO_2, sulphur, iodine, and HI.

Tin pyrites contains either SnS or SnS_2, or both, accompanied by sulphides of copper and iron.

Stannic sulphate, $Sn(SO_4)_2$, is left as a white mass when tin is boiled to dryness with sulphuric acid.

Stannic phosphate, $Sn_3(PO_4)_4$, is insoluble in nitric acid, and is sometimes used in separating phosphoric acid in quantitative analysis.

Stannic arsenate is left in the residue obtained by oxidising alloys containing tin and arsenic with nitric acid.

Tin is very closely connected with silicon by the composition, hardness, and insolubility of SnO_2, and by the characters of $SnCl_4$. Among metals it is conspicuous by the feebly basic character of its oxides and by the powerful reducing properties of $SnCl_2$.

254. Titanium (Ti=48 parts by weight), which stands in close chemical relationship to tin, used to be described as a very rare metal, but it has lately been found to exist in considerable quantity in iron ores and clays, although no very important practical application has hitherto been found for it. The form in which it is generally found is *titanic oxide* (or *anhydride*) (TiO_2), which occurs uncombined in the minerals *rutile*, *anatase*, and *brookite*, the first of which is isomorphous with tin-stone, and is extremely hard like that mineral.* In combination with oxide of iron, titanic oxide is found in *iron-sand*, *iserine*, or *menaccanite* (found originally at Menaccan in Cornwall), which resembles gunpowder in appearance, and is now imported in abundance from Nova Scotia and New Zealand. Some specimens of this mineral contain 40 per cent. of titanic oxide as ferrous titanate. To extract titanic oxide from it, the finely ground mineral is fused with three parts of potassium carbonate, when carbonic acid gas is expelled and potassium titanate formed; on washing the mass with hot water, this salt is decomposed, a part of its alkali being removed by the water, and an acid titanate left, mixed with the oxide of iron. This is dissolved in hydrochloric acid, and the solution evaporated to dryness, when the titanic oxide, and any silica which may be present, are converted into the insoluble modifications, and are left on digesting the residue again with dilute hydrochloric acid; the residue is washed with water (by decantation, for titanic oxide easily passes through the filter), dried, and fused at a gentle heat with bisulphate of potassium. This forms a soluble compound with the titanic oxide, which may be extracted by cold water, leaving the silica undissolved. The solution containing the titanic oxide is mixed with about twenty times its volume of water, and boiled for some time, when the titanic oxide is separated as a white precipitate, exhibiting a great disposition to cling as a film to the surface of the flask in which the solution is boiled, and giving it the appearance of being corroded. The titanic oxide becomes yellow when strongly heated, and white again on cooling; it does not dissolve in solution of potash like silica, but

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* The mineral *perowskite* is $CaO.TiO_2$.

when fused with potash it forms a titanate, which is decomposed by water; the acid titanate of potassium which is left may be dissolved in hydrochloric acid, and if the solution be neutralised with ammonium carbonate, hydrated titanic acid is precipitated, very much resembling alumina in appearance. By dissolving the gelatinous hydrate in cold hydrochloric acid, and dialysing, a solution of titanic acid in water is obtained, which is liable to gelatinise spontaneously if it contains more than 1 per cent. of the acid.

Titanic acid is employed in the manufacture of artificial teeth, and for imparting a straw-yellow tint to the glaze of porcelain.

If a mixture of titanic acid and charcoal be heated to redness in a porcelain tube, through which dry chlorine is passed, *titanium tetrachloride* ($TiCl_4$) is obtained as a colourless volatile liquid, very similar to tetrachloride of tin. By passing the vapour of the tetrachloride over heated sodium, the *metallic titanium* is obtained in prismatic crystals resembling specular iron ore in appearance. Like tin, it is said to dissolve in hydrochloric acid with liberation of hydrogen. The most remarkable chemical feature of titanium is its direct attraction for nitrogen, with which it combines when strongly heated in air. By passing ammonia gas over titanic oxide heated to redness, a yellow powder is formed, which is a nitride of titanium (Ti_2N_2). When suspended in water, it is blue by transmitted and yellow by reflected light. Ti_3N_4, corresponding to $TiCl_4$, is also known. Beautiful cubes of a copper colour and great hardness, formerly believed to be metallic titanium, are found adhering to the slags of blast furnaces in which titaniferous iron ores are smelted; these contain about 77 per cent. of titanium, 18 of nitrogen, and rather less than 4 of carbon, and are believed to consist of a compound of cyanide with nitride of titanium, $TiCy_2.3Ti_3N_2$. A similar compound is obtained by passing nitrogen over a mixture of titanic oxide and charcoal heated to whiteness.

Violet-coloured crystals of titanium trichloride ($TiCl_3$) are obtained by passing hydrogen charged with vapour of the tetrachloride through a red-hot porcelain tube; it forms a violet solution in water, which resembles stannous chloride in its reducing properties.

Titanium dichloride, $TiCl_2$, is obtained by heating the trichloride to dull redness in hydrogen. It is a black solid which quickly absorbs moisture, and takes fire if water be dropped upon it. When dissolved in water or alcohol, it evolves hydrogen from them. Bromine combines with it, causing much heat, and forming $TiCl_2Br_2$. The dichloride volatilises in hydrogen without fusing, and if cooled in hydrogen it occludes the gas, and takes fire on exposure to air. It glows when heated on platinum, evolving $TiCl_4$, and leaving a residue of TiO_2.

When a solution of titanic oxide (or acid titanate of potassium) in hydrochloric acid is acted on by zinc, a violet solution is formed, which deposits, after a time, a blue (or green) precipitate; this appears to be a *sesquioxide of titanium* (Ti_2O_3), and rapidly absorbs oxygen from the air, being converted into titanic oxide. This oxide is also obtained in the preparation of $TiCl_2$ unless air be very carefully excluded. It then forms small shining copper-coloured crystals with a violet reflection which have the same crystalline form as specular iron ore (Fe_2O_3). Ti_2O_3 is a basic oxide. The sulphate $Ti_2(SO_4)_3.8Aq$ crystallises from the violet solution obtained by dissolving titanium in sulphuric acid. Nitric acid oxidises it to *titanic sulphate*, $Ti(SO_4)_2.3Aq$, which forms a yellowish, transparent, deliquescent mass. The *potassio-titanic sulphate*, $K_2Ti(SO_4)_3.3Aq$, is formed when TiO_2 is fused with $KHSO_4$. A *titanous oxide* (TiO) is said to be obtained as a black powder when titanic oxide is strongly heated in a crucible lined with charcoal.

Titanium disulphide is not precipitated, like tin disulphide, when hydrosulphuric acid acts upon the tetrachloride; but if a mixture of the vapour of titanium tetrachloride with hydrosulphuric acid is passed through a red-hot tube, greenish-yellow scales of the disulphide, resembling mosaic gold, are deposited.

Titanium, like tin, is classed among the tetrad elements.

255. TUNGSTEN ($W = 184$) is chiefly found in the mineral *wolfram*, which occurs often associated with tin-stone, in large brown shining prismatic crystals, which are even heavier than tin-stone (sp. gr. 7.3), from which circumstance the metal derives its name, tungsten, in Swedish, meaning heavy stone. The symbol (W) used for tungsten is derived from the Latin name *wolframium*. Wolfram contains the tungstates of iron and manganese in somewhat variable proportions, but its general composition is expressed by the formula $3FeWO_4.MnWO_4$. *Scheelite*, tungstate of calcium ($CaWO_4$), is another mineral in which tungsten is found. A tungstate of copper has been found in Chili.

Tungstate of sodium is employed by calico-printers as a mordant, and is sometimes applied to muslin, in order to render it uninflammable. It is obtained by fusing wolfram with sodium carbonate, an operation to which tin ores containing this mineral in large quantity are sometimes submitted previously to smelting them. Water extracts the sodium tungstate, which may be crystallised in rhomboidal plates having the composition $Na_2WO_4.2Aq$. When a solution of this salt is mixed with an excess of hydrochloric acid, white *hydrated tungstic acid* ($H_2WO_4.Aq$) is precipitated, while hot solutions give a yellow precipitate of H_2WO_4; but if dilute hydrochloric acid be carefully added to a 5 per cent. solution of sodium tungstate in sufficient proportion to neutralise the alkali, and the solution be then dialysed (page 114), the sodium chloride passes through, and a pure aqueous solution of tungstic acid is left in the dialyser. This solution is unchanged by boiling, and when evaporated to dryness, it forms vitreous scales, like gelatin, which adhere very strongly to the dish. It redissolves in one-fourth of its weight of water, forming a solution of the very high specific gravity 3.2, which is, therefore, able to float glass. The solution has a bitter and astringent taste, and decomposes sodium carbonate with effervescence. It becomes green when exposed to air, from the de-oxidising action of organic dust. When tungstic acid is heated, it loses water, and becomes of a straw-yellow colour, and insoluble in acids. There are at least two modifications of tungstic acid, which bear to each other a relation similar to that between stannic and metastannic acids.

Barium tungstate has been employed as a substitute for white lead in painting.

The most characteristic property of tungstic acid is that of yielding a blue oxide ($WO_2.WO_3$), when placed in contact with hydrochloric acid and metallic zinc.

A very remarkable compound containing tungstic acid and soda is obtained when sodium ditungstate ($Na_2W_2O_7.4H_2O$) is fused with tin. If the fused mass be treated with strong potash, to remove free tungstic acid, washed with water, and treated with hydrochloric acid, yellow, lustrous, cubical crystals are obtained, which are remarkable, among sodium compounds, for their resistance to the action of water, of alkalies, and of all acids except hydrofluoric. The composition of these crystals appears to be $Na_2O.WO_2.2WO_3$. It is called *gold-bronze.* The corresponding potassium salt is *violet bronze*.

The *tungstoborates* are remarkable salts containing WO_3 and B_2O_3, combined with metallic oxides. Their solutions have a very high specific gravity; that of cadmium tungstoborate has the sp. gr. 3.6, and is used to effect the mechanical separation of minerals of different specific gravities. Thus, a diamond (sp. gr. 3.5) would float; whilst a white sapphire (sp. gr. 4.0) would sink in the solution.

The *tungsten dioxide* (WO_2) appears to be an indifferent oxide, and is obtained by reducing tungstic anhydride with hydrogen at a low red heat, when it forms a brown powder which is dissolved by boiling in solution of potash, hydrogen being evolved, and potassium tungstate formed.

Metallic tungsten is obtained by reducing tungstic anhydride with charcoal at a white heat, as an iron-grey infusible metal of sp. gr. 17.6, very hard, not affected by hydrochloric or diluted sulphuric acid, but converted into tungstic acid by the action of nitric acid. When tungsten is dissolved in about ten times its weight of fused steel, it forms an extremely hard alloy.

When tungsten is heated in chlorine, the *tungstic chloride* (WCl_6) sublimes in bronze-coloured needles. When gently heated in hydrogen, it is converted into the tetrachloride (WCl_4), but if its vapour be mixed with hydrogen and passed through a glass tube heated to redness, metallic tungsten is obtained in a form in which it is not dissolved even by aqua regia, though it may be converted into potassium tungstate by potassium hypochlorite mixed with potash in excess. WCl_6 is also obtained in steel-blue needles, together with $WOCl_4$ and WO_2Cl_2 by the action of PCl_5 on WO_3.

Tungsten disulphide (WS_2) is a black crystalline substance resembling plumbago, obtained by heating a mixture of potassium ditungstate with sulphur, and washing with hot water. *Tungsten trisulphide* (WS_3) is a sulphur-acid, obtainable as a brown precipitate by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid.

256. *Niobium* (Nb = 94) (formerly called *columbium*) has been obtained from a rare dark grey, hard, crystalline mineral known as *columbite*, occurring in Massa-

chusetts. This mineral contains *niobic oxide* (Nb_2O_5) combined with the oxides of iron and manganese.

The niobic oxide is extracted by a laborious process, and forms a white powder, sparingly soluble in hydrochloric acid. Niobium itself has been obtained as a lustrous steel-grey powder insoluble in nitric acid and in aqua regia, but dissolved by a mixture of nitric and hydrofluoric acids, and by strong sulphuric acid. When heated in air, it burns to Nb_2O_5. It forms two chlorides, $NbCl_3$ and $NbCl_5$, and some remarkable crystalline compounds containing niobium, carbon, and nitrogen. Niobic oxide is an acid oxide. Yttrium niobate, $Y_2O_3.Nb_2O_5$, forms the mineral *Fergusonite*. Other mineral niobates are *Euxenite*, *Samarskite*, *Hatchettolite*, and *Rogersite*.

Tantalum, formerly believed to be identical with niobium, occurs in the *tantalite* and *yttrotantalite* of Sweden, which contain *tantalic oxide* (Ta_2O_5) combined with ferrous and manganous oxides.

Niobium and tantalum have recently been found to the amount of 2 or 3 per cent. in the tin ore of Montebras. The compounds of niobium and tantalum resemble each other very closely.

COPPER.

$Cu'' = 63.5$ parts by weight.

257. Metallic copper is met with in nature more abundantly than *metallic* iron, though the compounds of the latter metal are of more frequent occurrence than those of the former.* A very important vein of metallic copper, of excellent quality, occurs near Lake Superior in North America, from which 6000 tons were extracted in 1858. Metallic copper is also sometimes found in Cornwall, and *copper sand*, containing metallic copper and quartz, is imported from Chili.

Ores of copper.—The most important English ore of copper is *copper pyrites*, which is a double sulphide, containing copper, iron, and sulphur in the proportions indicated by the formula $CuFeS_2$. It may be known by its beautiful brass-yellow colour and metallic lustre. Copper pyrites is found in Cornwall and Devonshire, and is generally associated with arsenical pyrites ($FeS_2.FeAs_2$), tin-stone (SnO_2), quartz, fluor spar, and clay. A very attractive variety of copper pyrites is called *variegated copper ore* or *peacock copper*, in allusion to its rainbow colours; its simplest formula is Cu_3FeS_3. This variety is found in Cornwall and Killarney.

Copper glance (Cu_2S) is another Cornish ore of copper, of a dark grey colour and feeble metallic lustre.

Grey copper ore, also abundant in Cornwall, is essentially a compound of the sulphides of copper and iron with those of antimony and arsenic, but it often contains silver, lead, zinc, and sometimes mercury.

Malachite, a basic carbonate of copper, is imported from Australia (Burra Burra), and is also found abundantly in Siberia. Green malachite, the most beautifully veined ornamental variety, has the composition $CuCO_3.Cu(OH)_2$, and blue malachite is $2CuCO_3.Cu(OH)_2$.

Red copper ore (Cu_2O) is found in West Cornwall, and the black oxide (CuO) is abundant in the north of Chili.

258. The seat of English copper-smelting is at Swansea, which is situated in convenient proximity to the anthracite coal employed in the

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* Copper is not at all frequently found in animals or vegetables; but Church has made the remarkable observation that the red colouring matter (*turacine*) of the feathers of the plantain-eater (*touraco*) contains as much as 5.9 per cent. of copper. It has also been found in the blood of the cuttle-fish, as *hæmocyanin*, which is blue in its oxidised condition in the arterial blood, and colourless in the venous blood.

furnaces. The chemical process by which copper is extracted from the ore includes three distinct operations—(1) the *roasting*, to expel the arsenic and part of the sulphur, and to convert the sulphide of iron into oxide of iron; (2) the *fusing with silica*, to remove the oxide of iron as silicate, and to obtain the copper in combination with sulphur only; and (3) the *roasting* of this combination of copper with sulphur, in order to expel the latter and obtain metallic copper.

The details of the smelting process appear somewhat complicated, because it is divided into several stages to allow of the introduction of the different varieties of ore to be treated. Thus, the first roasting process is unnecessary for the oxides and carbonates of copper, and the fusion with silica is not needed for those ores which are free from iron, so that they may be introduced at a later stage in the operations.

(1) *Calcining or roasting the ore to expel arsenic and part of the sulphur.*—The ores having been sorted, and broken into small pieces, are mixed so as to contain from 8 to 10 per cent. of copper, and roasted, in quantities of about three tons, for at least twelve hours, on the spacious hearth (H, fig. 248) of a reverberatory furnace (fig. 247) at a temperature insufficient for fusion, being occasionally stirred to expose them freely to the action of the air, which is admitted into the furnace through an opening (O) in the side of the hearth upon which the ore is spread. The oxygen of the air converts a part of the sulphur into SO_2, and the bulk of the As into As_2O_3, which passes off in the form of vapour. A part of the sulphide of iron is converted into ferrous sulphate ($FeSO_4$) by absorbing oxygen at an early stage of the process, and this sulphate is afterwards decomposed at a higher temperature, evolving SO_2 and SO_3, and leaving oxide of iron. A portion of the sulphide of copper is also converted into oxide of copper during the roasting, so that the roasted ore consists essentially of a mixture of oxide and sulphide of copper with oxide and sulphide of iron. Since the sulphide of iron is more easily oxidised than sulphide of copper, the greater part of the latter remains unaltered in the roasted ore.

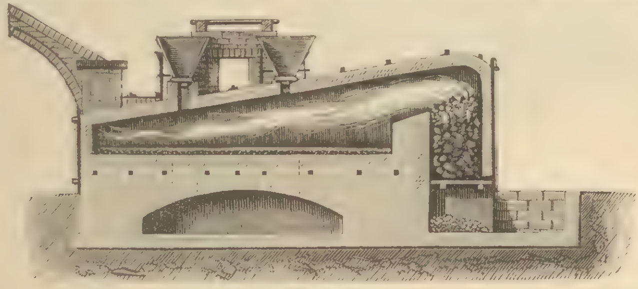
Fig. 247.

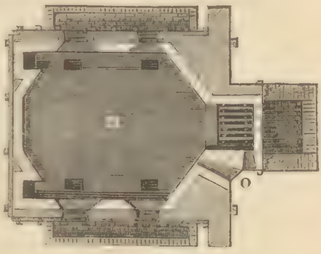

Fig. 248.

During the roasting of copper ore dense white fumes escape from the furnaces. This *copper smoke*, as it is termed, contains As_2O_3, SO_2, SO_3.

and HF, the latter being derived from the fluor spar associated with the ore; if allowed to escape, these fumes seriously contaminate the air in the neighbourhood, so that they are usually condensed in flues and *rain-chambers* by showers of water.

(2) *Fusion for coarse metal to remove the oxide of iron by dissolving it with silica at a high temperature.*—The roasted ore is now mixed with *metal slag* from process 4, and with ores containing silica and oxides of copper, but no sulphur; the mixture is introduced into the *ore furnace* (fig. 249), and fused for five hours at a higher temperature than that employed in the previous operation. In this process fluor spar is sometimes added in order to increase the fluidity of the slag.

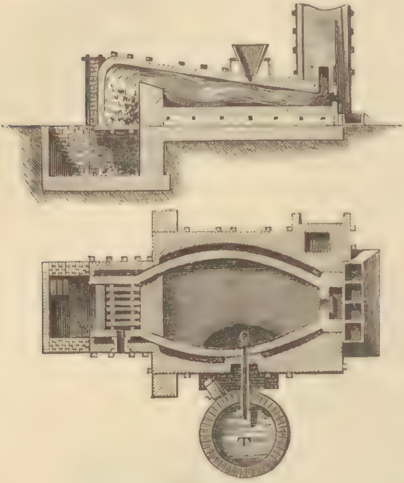

Fig. 249.

The oxide of copper acts upon the sulphide of iron still contained in the roasted ore, with formation of sulphide of copper and oxide of iron, but since there is more sulphide of iron present than the oxide of copper can decompose, the excess of sulphide of iron combines with the sulphide of copper to form a fusible compound, which separates from the slag, and collects in the form a *matt* or *regulus* of *coarse metal*, in a cavity (C) on the hearth of the furnace: it is run out into a tank of water (T) in order to granulate it, so that it may be better fitted to undergo the next operation.

The oxide of iron combines with the silica contained in the charge, to form a fusible ferrous silicate (*ore-furnace slag*), which is raked out into moulds of sand, and cast into blocks used for rough building purposes in the neighbourhood.

The composition of the coarse metal corresponds pretty closely with the formula $CuFeS_2$. It contains from 33 to 35 per cent. of copper; whilst the original ore, before roasting, is usually sorted so that it may contain about 8.5 per cent.

The ore-furnace *slag* is approximately represented by the formula $FeO.SiO_2$; but it contains a minute proportion of copper, as is shown by the green efflorescence on the walls in which it is used around Swansea. Fragments of quartz are seen disseminated through this slag.

(3) *Calcination of the coarse metal to convert the greater part of the sulphide of iron into oxide.*—The granulated coarse metal is roasted at a moderate temperature for twenty-four hours, as in the first operation, so that the oxygen of the air may decompose the sulphide of iron, removing the sulphur as sulphurous acid, and leaving the iron in the form of oxide.

(4) *Fusion for white metal to remove the whole of the iron as silicate.*—The roasted coarse metal is mixed with *roaster* and *refinery* slags from

processes 5 and 6, and with ores containing carbonates and oxides of copper, and fused for six hours, as in the second operation. Any sulphide of iron which was left unchanged in the roasting is now converted into oxide of iron by the oxide of copper, the latter metal taking the sulphur. The whole of the oxide of iron combines with the silica to form a fusible slag, the composition of which is approximately represented by the formula $3FeO.2SiO_2$.

The *matt* or *regulus* of *white metal*, which collects beneath the slag, is nearly pure cuprous sulphide (Cu_2S), half the sulphur existing in the cupric sulphide (CuS) having been removed by oxidation in the furnace. The white metal is run into sand-moulds and cast into ingots. The tin and other foreign metals usually collect in the lower part of the ingot, so that, for making *best selected copper*, the upper part is broken off and worked separately, the inferior copper obtained from the lower part of the ingot being termed *tile-copper*. The ingots of white metal often contain beautiful tufts of metallic copper in the form of *copper moss*.

The slag separated from the white metal (*metal slag*) is much more fluid than the ore-furnace slag, and contains so much silicate of copper that it is preserved for use in the melting for coarse metal.

(5) *Roasting the white metal to remove the sulphur and obtain blister copper.*—The ingots of white metal (to the amount of about 3 tons) are placed upon the hearth of a reverberatory furnace, and heated for four hours to a temperature just below fusion, so that they may be oxidised at the surface, the sulphur passing off as sulphurous acid gas, and the copper being converted into oxide. During this roasting the greater part of the arsenic, generally present in the fine metal, is expelled as As_2O_3. The temperature is then raised, so that the charge may be completely fused, after which it is lowered again till the twelfth hour. The oxide of copper now acts upon the sulphide of copper to form metallic copper and sulphurous acid gas, which escapes, with violent ebullition, from the melted mass; $Cu_2S + 2CuO = SO_2 + Cu_4$. When this ebullition ceases, the temperature is again raised so as to cause the complete separation of the copper from the slag, and the metal is run out into moulds of sand. Its name of *blister copper* is derived from the appearance caused by the escape of the last portions of SO_2 from the metal when solidifying in the mould.

The slag (*roaster slag*) is formed in this operation by the combination of a part of the oxide of copper with silica derived from the sand adhering to the ingots, and from the hearth of the furnace. The slag also contains the silicates of iron and of other metals, such as tin and lead, which might have been contained in the white metal. This slag is used again in the melting for white metal.

(6) *Refining to remove foreign metals.*—This process consists in slowly fusing 7 or 8 tons of the blister copper in a reverberatory furnace, so that the air passing through the furnace may remove any remaining sulphur as sulphurous acid gas, and may oxidise the small quantities of iron, tin, lead, &c., present in the metal. Of course, a large proportion of the copper is oxidised at the same time, and the cuprous oxide, together with the oxides of the foreign metals, combine with silica (from the hearth or from adhering sand) to form a slag which collects upon the surface of the melted copper. A portion of the cuprous oxide is dissolved by the metallic copper, rendering it brittle or *dry copper*.

(7) *Toughening or poling, to remove a part of the oxygen and bring the copper to tough-pitch.*—After about twenty hours the slag is skimmed from the metal, a quantity of anthracite is thrown over the surface to prevent further oxidation, and the metal is *poled*, *i.e.*, stirred with a pole of young wood, until a small sample, removed for examination, presents a peculiar silky fracture, indicating it to be at *tough-pitch*, when it is cast into ingots.

The chemical change during the poling appears to consist in the removal of the oxygen contained in the cuprous oxide present in the metal, by the reducing action of the combustible gases disengaged from the wood. The presence of a small proportion of cuprous oxide is said to confer greater toughness upon the metal, so that if the poling be continued until the whole of the oxygen is removed, *over-poled copper* of lower tenacity is obtained. On the other hand, the brittleness of *under-poled copper* is due to the presence of cuprous oxide in too large proportion. *Tough-cake copper* is that which has been poled to the proper extent.

The addition of about 0.07 per cent. of phosphorus, as copper phosphide, before the final poling, shortens the process and increases the density of the metal. The copper phosphide is made by dissolving about 7 per cent. of phosphorus in melted copper.

When the copper is intended for rolling, a small quantity (not exceeding ½ per cent.) of lead is generally added to it before it is ladled into the ingot moulds. Apparently the oxide of lead formed by the action of the air assists in removing some of the impurities in the form of slag (*scorification*).

The chemical changes which take place during the above processes will be more clearly understood after inspecting the subjoined table, which exhibits the composition of the products obtained at different stages of the process, these being distinguished by the same numerals as were employed in the above description.

Products obtained in smelting Ores of Copper.

In 100 parts.	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	White Metal.	Blister Copper.	Refined Copper.	Tough-pitch Copper.
		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Copper . . .	8.2	8.6	33·7	33·7	77·4	98.0	99·4	99.6
Iron . . .	17·9	17.6	33·6	33·6	0.7	0.5	trace	trace
Sulphur . . .	19.9	12.5	29.2	13.0	21.0	0.2	trace	trace
Oxygen . . .	1.0	4·5	...	11.0	...	...	0.4	0.03
Silica . . .	34·3	34·3						
Slags.			**Ore Furnace**		**Metal.**	**Roaster.**	**Refinery**	
			(2)		(4)	(5)	(6)	
Oxide of iron (FeO)			54.0	...	56.0	28.0	3.1	
Suboxide of copper (Cu_2O) . .			0.5	...	0.9	16.9	39.2	
Silica			45·0	...	33·8	47·5	47·4	

Blue metal is the term applied to the regulus of white metal (from process 4) when it still contains a considerable proportion of sulphide of iron, in consequence of a deficient supply of oxide of copper in the furnace. *Pimple metal* is obtained in the same operation when the oxide of copper is in excess, so that a portion of the copper is reduced, as in process 5, with evolution of sulphurous acid gas, which produces the pimply appearance in escaping. The reduced copper gives a reddish colour to the pimple copper. *Coarse copper* is a similar intermediate stage between white metal and blistered copper. *Tile copper* is that extracted from the bottoms of the ingots of white metal, when the tops have been detached for making best select copper. *Rosette* or *rose copper* is obtained by running water upon the toughened metal, so as to enable the metal to be removed in films. *Anglesea* or *Mona copper* is a very tough copper, reduced by metallic iron from the *blue water* of the copper mines, which contains sulphate of copper.

A new method (*Hollway's process*) has recently been proposed for the treatment of cupreous pyrites, which consists in blowing air through it in a melted state in a Bessemer's converter (p. 322), when the combustion of the sulphur maintains a very high temperature, and the bulk of the copper sinks to the bottom as a regulus, containing comparatively small quantities of iron and sulphur, whilst the iron is converted into oxide, which forms a slag with silica, added for that purpose. The copper regulus contains all the silver and gold present in the pyrites. It is proposed to utilise the SO_2 resulting from the combustion of the sulphur, by converting it into H_2SO_4.

Much copper is extracted from the *spent pyrites* of the vitriol works (p. 203), which sometimes yields about 3 per cent. It is converted into chloride by roasting the pyrites with common salt; the chloride is dissolved out by water and the copper precipitated in the metallic state by iron.

259. For the purpose of illustration, copper may be extracted from copper pyrites on the small scale in the following manner:—

200 grains of the powdered ore are mixed with an equal weight of dried borax, and fused in a covered earthen crucible (of about 8 oz. capacity), at a full red heat for about half an hour. The earthy matters associated with the ore are dissolved by the borax, and the pure copper pyrites collects at the bottom of the crucible. The contents of the latter are poured into an iron mould (scorifying mould, fig. 250), and when the mass has set, it is dipped into water. The semi-metallic button is then easily detached from the slag by a gentle blow; it is weighed, finely powdered in an iron mortar, and introduced into an earthen crucible, which is placed obliquely over a dull fire, so that it may not become hot enough to fuse the ore, which should be stirred occasionally with an iron rod to promote the oxidation of the sulphur by the air. When the odour of SO_2 is no longer perceptible, the crucible is placed in a Sefström's blast-furnace (fig. 244), and exposed for a few minutes to a bright red heat, in order to decompose the sulphates of iron and copper. When no more white fumes of SO_3 are perceived, the crucible is lifted from the fire, held over the iron mortar, and the roasted ore quickly scraped out of it with a steel spatula. This mixture of the oxides of copper and iron is reduced to a fine powder, mixed with 600 grains of dried carbonate of soda and 60 grains of powdered charcoal, returned to the same crucible, covered with 200 grains of dried borax, and heated in a Sefström's furnace for twenty minutes. The crucible is then allowed to cool, and carefully broken to extract the button of metallic copper, which is weighed to ascertain the amount contained in the original ore.

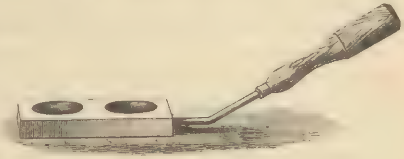

Fig. 250.

260. *Effect of impurities upon the quality of copper.*—The information possessed by chemists upon this subject is still very limited. It has been already mentioned that the presence of a small proportion of *cuprous oxide* in commercial copper is found to increase its toughness. It is believed that copper, perfectly free from metallic impurities, is not improved in quality by the presence of the oxide, but that this substance has the effect of counteracting the red-shortness (see p. 323) of commercial copper, caused by the presence of foreign metals.

Sulphur, even in minute proportion, appears seriously to injure the malleability of copper. *Arsenic* is almost invariably present in copper, very frequently amounting to 0.1 per cent., and does not appear to exercise any injurious influence in this proportion; indeed, its presence is sometimes stated to increase the malleability and tenacity of the metal. *Phosphorus* is not usually found in the copper of commerce. When purposely added in quantity varying from 0.12 to 0.5 per cent., it is found to increase the hardness and tenacity of the copper, though rendering it somewhat red-short.

Tin, in minute proportion, is also said to increase the toughness of copper, though any considerable proportion renders it brittle. *Antimony* is a very objectionable impurity, and is by no means uncommon in samples of copper. *Nickel* is believed to injure the quality of copper in which it occurs. *Bismuth* and *silver* are very generally found in marketable copper, but their effect upon its quality has not been clearly determined. All impurities appear to affect the malleability and tenacity of copper more perceptibly at high than at low temperatures.

The conducting power of copper for electricity is affected in an extraordinary degree by the presence of impurities. Thus, if the conducting power of chemically pure copper be represented by 100, that of the very pure native copper from Lake Superior has been found to be 93, that of the copper extracted from the malachite of the Burra Burra mines in South Australia was 89, whilst that of Spanish copper, remarkable for containing much arsenic, was only 14.

Pure copper is obtained by decomposing a solution of pure sulphate of copper by the galvanic current, as in the *electrotype* process. If the negative wire be attached to a copper plate immersed in the solution, the pure copper may be stripped off this plate in a sheet.

261. PROPERTIES OF COPPER.—The most prominent character which confers upon copper so high a rank among the useful metals is its malleability, which allows it to be readily fashioned under the hammer, and to be beaten or rolled out into thin sheets; among the metals in ordinary use, only gold and silver exceed copper in malleability, and the comparative scarcity of those metals leads to the application of copper for most purposes where great malleability is requisite.

Although, in tenacity or strength, copper ranks next to iron, it is still very far inferior to it, for a copper wire of $\frac{1}{10}$th inch in diameter will support only 385 lbs., while a similar iron wire will carry 705 lbs. without breaking; and, in consequence of its inferior tenacity, copper is less ductile than iron, and does not admit of being so readily drawn into exceedingly thin wires.

The comparative ease with which copper may be fused allows it to be cast much more readily than iron; for it will be remembered that the latter metal can be liquefied only by the highest attainable furnace heat, whereas copper can be fused at about 1300° C. (2372° F.), a temperature generally spoken of as a bright red heat.

As being one of the most sonorous of metals, copper has been, from time immemorial, employed in the construction of bells and musical instruments. The readiness with which it transmits electricity is turned to account in telegraphic communication, its conducting power being almost equal to that of silver, which is the best of electric conductors. In conducting power for heat, copper is surpassed only by silver and gold.

Copper is not so hard as iron, and is somewhat heavier, the specific gravity of cast copper being 8.92, and that of hammered or drawn copper 8.95.

The resistance of copper to the chemical action of moist air gives it a great advantage over iron for many uses, and the circumstance that it does not decompose water in presence of acids enables it to be employed as the negative plate in galvanic couples.

262. *Effect of sea water upon copper.*—When copper is placed in a solution of salt in water, no perceptible action takes place; but in the course of time, if the air be allowed access, it becomes covered with a green coating of *oxychloride of copper* ($CuCl_2.3CuO.4H_2O$), the action probably consisting, first, in the conversion of the copper into oxide by the air, and afterwards in the decomposition of the oxide by the sodium chloride; $4CuO + 2NaCl + H_2O = CuCl_2.3CuO + 2NaHO$. The surface of the copper is thus corroded, and in the case of a copper-bottomed ship, the action of sea water not only occasions a great waste of copper, but roughens the surface of the sheathing, and affords points of attachment to barnacles, &c., which injure the speed of the vessel. Many attempts have been made to obviate this inconvenience. Zinc has been fastened here and there to the outside of the copper, placing the latter in an electro-negative condition; the copper has been coated with various compositions, but with very indifferent success. *Muntz metal*, or *yellow sheathing*, or *malleable brass*, an alloy of 3 parts of copper and 2 parts of zinc, has been employed with some advantage in place of copper, for it is very much cheaper and somewhat less easily corroded; but the difficulty is by no means overcome. Copper containing about 0.5 per cent. of phosphorus is said to be corroded by sea water much less easily than pure copper.

263. *Danger attending the use of copper vessels in cooking food.*—The use of copper for culinary vessels has occasionally led to serious consequences, from the poisonous nature of its compounds, and from ignorance of the conditions under which these compounds are formed. A perfectly clean surface of metallic copper is not affected by any of the substances employed in the preparation of food, but if the metal has been allowed to remain exposed to the action of the air, it becomes covered with a film of oxide of copper, and this subsequently combines with water and carbonic acid gas derived from the air to produce a basic carbonate of copper,* which, becoming dissolved, or mixed with the food prepared in these vessels, confers upon it a poisonous character. This danger may be avoided by the use of vessels which are perfectly clean and bright, but even from these, certain articles of food may become contaminated with copper, for this metal is much more likely to be oxidised by the air when in contact with acids (vinegar, juices of fruits, &c.), or with fatty matters, or even with common salt; and if oxide of copper be once formed, it will be readily dissolved by such substances. Hence it is usual to coat the interior of copper vessels with tin, which is able to resist the action of the air, even in the presence of acids and saline matters.

264. USEFUL ALLOYS OF COPPER WITH OTHER METALS.—Copper forms a greater number of useful alloys than any other metal. With about one-sixth of its weight of *tin*, it forms the *hard bronze* which was used for weapons before the art of working iron was well known. With one-tenth

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* Often erroneously called *verdigris*, which is really a basic acetate of copper.

of its weight of tin, it yields *gun metal*, remarkable for its strength. With from one-third to one-fourth of its weight of tin, it yields the elastic sonorous alloy used as *bell metal*. With half its weight of tin, it gives the extremely hard, brittle, silvery *speculum metal* used in reflecting telescopes. *Bronze for statues* has sometimes the same composition as gun metal, but often contains a large proportion of zinc. *Phosphor-bronze*, remarkable for its hardness and toughness, is an alloy of copper containing about 10 per cent. of tin and 1 or 2 per cent. of phosphorus, which is added to the melted copper in the form of tin phosphide. With from one-third to one-half its weight of *zinc*, copper forms brass, much harder than copper, and capable of being hammered into thin leaves as a substitute for gold. The most important alloys of which copper is a predominant constituent are the following :—

Brass—64 copper, 36 zinc.
Muntz metal—60 to 64 copper, 40 to 36 zinc.
German silver—51 copper, 30.5 zinc, 18.5 nickel.
Aich or Gedge's metal—60 copper, 38.2 zinc, 1.8 iron.
Sterro metal—55 copper, 42.4 zinc, 0.8 tin, 1.8 iron.
Bell metal—78 copper, 22 tin.
Speculum metal—66.6 copper, 33.4 tin.
Bronze—80 copper, 4 tin, 16 zinc.
Gun metal—90.5 copper, 9.5 tin.
Bronze coinage—95 copper, 1 zinc, 4 tin.
Aluminium bronze—90 copper, 10 aluminium.

Brass is made by melting copper in a crucible, and adding rather more than half its weight of zinc. It is difficult to decide whether brass is a true chemical compound or a mere mechanical mixture of copper and zinc, because it is capable of dissolving either of those metals when in a state of fusion. The circumstance that it can be deposited by decomposing a solution containing copper and zinc by the galvanic current, would appear to indicate that it is a chemical compound, and its physical properties are not such as would be expected from a mere mixture of its constituents. A small quantity of tin is added to brass intended for door-plates, which renders the engraving much easier. When it has to be turned or filed, about 2 per cent. of lead is usually added to it, in order to prevent it from adhering to the tools employed. Brass cannot be melted without losing a portion of its zinc in the form of vapour. When exposed to frequent vibration (as in the suspending chains of chandeliers), it suffers an alteration in structure and becomes extremely brittle. The solder used by braziers consists of equal weights of copper and zinc. In order to prevent ornamental brass-work from being tarnished by the action of air, it is either lacquered or bronzed. *Lacquering* consists simply in varnishing the brass with a solution of shellac in spirit, coloured with dragon's blood. *Bronzing* is effected by applying a solution of arsenic or mercury, or platinum, to the surface of the brass. By the action of arsenious oxide dissolved in hydrochloric acid, upon brass, the latter acquires a coating composed of arsenic and copper, which imparts a bronzed appearance, the zinc being dissolved in place of the arsenic, which combines with the copper at the surface. A mixture of corrosive sublimate (mercuric chloride, $HgCl_2$) and acetic acid is also sometimes employed, when the mercury is displaced by the zinc, and precipitated upon the surface of the brass, with which it forms a bronze-like amalgam. For bronzing brass instruments, such as theodolites, levels, &c., a solution of chloride of platinum is employed, the zinc of the brass precipitating a very durable film of metallic platinum upon its surface ($PtCl_4 + Zn_2 = Pt + 2ZnCl_2$). *Aich metal* is a kind of brass containing iron, and has been employed for cannon, on account of its great strength. At a red heat it is very malleable.

Sterro-metal (στεῤῥός, strong) is another variety of brass containing iron and tin, said to have been discovered accidentally in making brass with the alloy of zinc and iron obtained during the process of making galvanised iron (page 290). It possesses great strength and elasticity, and is used by engineers for the pumps of hydraulic presses.

Aluminium bronze has been already noticed, and the alloys of copper and tin have been described under the latter metal.

A very hard white alloy of 77 parts of zinc, 17 of tin, and 6 of copper, is sometimes employed for the bearings of the driving-wheels of locomotives.

Iron and steel are coated with a closely adherent film of copper, by placing them in contact with metallic zinc in an alkaline solution of oxide of copper, prepared by mixing sulphate of copper with tartrate of potash and soda, and caustic soda. The copper is thus precipitated upon the iron by slow voltaic action, the zinc being the attacked metal. By adding a solution of stannate of soda to the alkaline copper solution, a deposit of bronze may be obtained.

265. OXIDES OF COPPER.—Two oxides of copper are well known in the separate state, viz., the suboxide, Cu_2O, and the oxide, CuO. Another oxide, Cu_4O, has been obtained in a hydrated state, and there is some evidence of the existence of an acid oxide.

The *black oxide of copper* (*cupric oxide*), CuO, is employed by the chemist in the ultimate analysis of organic substances by combustion, being prepared for this purpose by acting upon copper with nitric acid to convert it into cupric nitrate (page 136), and heating this to dull redness in a rough vessel made of sheet copper, when it leaves the black oxide; $Cu(NO_3)_2 = 2NO_2 + O + CuO$. At a higher temperature the oxide fuses into a very hard mass; it evolves very little oxygen when strongly heated. Oxide of copper absorbs water easily from the air, but it is not dissolved by water; acids, however, dissolve it, forming the salts of copper, whence the use of oil of vitriol and nitric acid for cleansing the tarnished surface of copper; a blackened coin, for example, immersed in strong nitric acid, and thoroughly washed, becomes as bright as when freshly coined. Silica dissolves oxide of copper at a high temperature, forming cupric silicate, which is taken advantage of in producing a fine green colour in glass.

Red oxide or *suboxide of copper* (*cuprous oxide*), Cu_2O, is found crystallised in regular octahedra, and is formed when copper is heated in air, that portion of the *copper-scale* which is in contact with the air becoming CuO, while that in contact with the metal is Cu_2O. It is made by heating a mixture of 5 parts of the black oxide with 4 parts of copper filings in a closed crucible. It may also be prepared by boiling a solution of cupric sulphate with a solution containing sodium sulphite and sodium carbonate in equal quantities, when the cuprous oxide is precipitated as a reddish-yellow powder, which should be washed, by decantation, with boiled water—

$$2CuSO_4 + 2Na_2CO_3 + Na_2SO_3 = Cu_2O + 3Na_2SO_4 + 2CO_2.$$

Cu_2O is precipitated in minute octahedral crystals when solution of $CuSO_4$ mixed with glucose is boiled with excess of potash.

Cuprous oxide is a feeble base, but its salts are not easily obtained by direct action of acids, for these generally decompose it into metallic copper and cupric oxide, yielding cupric salts. In the moist state it is slowly oxidised by the air. Ammonia dissolves cuprous oxide, forming a solution which is perfectly colourless until it is allowed to come into contact with air, when it assumes a fine blue colour, becoming converted into an ammoniacal solution of cupric oxide. If the blue solution be placed in a stoppered bottle (quite filled with it) with a strip of clean copper, it will gradually become colourless, the cupric oxide being again reduced to cuprous oxide, a portion of the copper being dissolved. When copper filings are shaken with ammonia in a bottle of air, the same blue solution is obtained, the oxidation of the copper being attended with a simultaneous oxidation of a portion of the ammonia, and its conversion into nitrous acid, so that the white fumes of ammonium nitrite are formed in the upper part of the bottle. If the blue solution be poured into a large quantity of water, a light blue precipitate of cupric hydrate is obtained. The ammoniacal solution of cupric oxide has the unusual property of dissolving paper, cotton, tow, and other varieties of *cellulose*, this substance being reprecipitated from the solution on adding an acid.

Cuprous oxide, added to glass, imparts to it a fine red colour, which is turned to account by the glass-maker.

Quadrant oxide of copper, Cu_4O, has been obtained in combination with water, by the action of stannous chloride and potash upon a cupric salt.

Cuprous hydride, Cu_2H_2, is precipitated when cupric sulphate is heated with hypophosphorous acid; or a strong solution of cupric sulphate may be strongly acidulated with dilute sulphuric acid, solution of sodium hypophosphite added, and heated till a brown precipitate forms; this is the hydride, which must not be further heated, as it is decomposed into its elements at 60° C. Hydrochloric acid dissolves it easily, with brisk effervescence from escape of hydrogen, and formation of a colourless solution of cuprous chloride—

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

This reaction is regarded as supporting the belief that two atoms of H unite to form a molecule.

Cuprous hydrate, $4Cu_2O.H_2O$, is obtained as a yellow precipitate when a solution of a cuprous salt is added to excess of potash. If air be excluded, it may be dried at 100° C. without decomposition. Air oxidises it to cupric hydrate. With ammonia it behaves like cuprous oxide.

Cupric hydrate, $Cu(HO)_2$, is obtained as a blue precipitate when potash or soda is added to a cupric salt. When boiled in the liquid, it becomes black CuO, but if it be allowed to dry over sulphuric acid, it may be heated to 100° C. without decomposition. Its solubility in ammonia and the properties of the solution have been noticed above. In the presence of tartaric acid, sugar, and many other organic substances, cupric hydrate dissolves in caustic potash and soda, forming dark blue solutions. The paint known as *blue verditer* is cupric hydrate obtained by decomposing cupric nitrate with calcium hydrate.

Cupric acid is believed to be formed when metallic copper is fused with nitre and caustic potash. The mass yields a blue solution in water, which is very easily decomposed with evolution of oxygen and precipitation of cupric oxide. The existence of an unstable oxide of copper, containing more than one atom of oxygen, is also rendered probable by the circumstance that oxide of copper acts like manganese dioxide in facilitating the disengagement of oxygen from potassium chlorate by heat (page 34).

Cuprous nitride, Cu_6N_2, is formed by passing ammonia over CuO at 250° C. It is a dark green powder which decomposes at a high temperature, *evolving* heat.

Cupric nitrate, $Cu(NO_3)_2.3Aq$, crystallises in blue prisms from a solution of copper in nitric acid. It is deliquescent and soluble in water and alcohol. When heated to 65° C., it becomes a green *basic nitrate*, $Cu(NO_3)_2.3Cu(HO)_2$. Cupric nitrate is used as an oxidising agent in dyeing and calico-printing. Cupric ammonio-nitrate, $Cu(NO_3)_2.4NH_3$, is deposited in dark blue crystals from a mixture of cupric nitrate with excess of ammonia.

266. *Sulphate of copper*, or *cupric sulphate*.—The beautiful prismatic crystals known as *blue vitriol*, *blue stone*, *blue copperas*, or sulphate of copper, have been already mentioned as formed from the residue in the preparation of sulphurous acid gas (page 197), by dissolving copper in oil of vitriol, a process which is occasionally employed for the manufacture of this salt. A considerable supply of the sulphate is obtained as a secondary product in the process of silver-refining (page 207).

The sulphate of copper is also manufactured by roasting copper pyrites ($FeCuS_2$) with free access of air, when it becomes partly converted into a mixture of cupric sulphate with ferrous sulphate; $FeCuS_2 + O_8 = FeSO_4 + CuSO_4$. The ferrous sulphate, however, is decomposed by the heat, leaving ferric oxide (see page 210). When the roasted mass is treated with water, the ferric oxide is left undissolved, but the cupric sulphate enters into solution, and may be obtained in crystals by evaporation.

Since ferrous sulphate and cupric sulphate are isomorphous, they crystallise together, and can be separated only by converting the ferrous into ferric sulphate by an oxidising agent such as nitric acid.

The crystals, as they are found in commerce, are usually opaque, but if they are dissolved in hot water and allowed to crystallise slowly, they become perfectly transparent, and have then the composition expressed by the formula $CuSO_4.5H_2O$. If the crystals be heated to the temperature of boiling water, they lose four-fifths of their water, and crumble down to a greyish-white powder, which has the composition $CuSO_4.H_2O$, and if this be moistened with water, it becomes very hot and resumes its original blue colour. The whitish opacity of the ordinary crystals of blue stone is due to the absence of a portion of the water of crystallisation. The fifth molecule of water can be expelled only at a temperature of nearly 200° C., and is therefore generally called water of constitution (see page 44), the formula of the crystals being then written $CuSO_4.H_2O.4Aq$. The crystals dissolve in 4 parts of cold and 2 parts of boiling water. The solution reddens litmus.

The sulphate of copper is largely employed by the dyer and calico-printer, and in the manufacture of pigments. It is also occasionally used in medicine, in the electrotype process, and in galvanic batteries.

When ammonia is added to solution of cupric sulphate, a basic sulphate is first precipitated, which is dissolved by an excess of ammonia to a dark blue fluid. On allowing this to evaporate, dark blue crystals of *ammonio-cupric sulphate*, $CuSO_4.4NH_3.H_2O$, are deposited. They lose their ammonia when exposed to the air.

A *basic cupric sulphate*, $CuSO_4.3Cu(OH)_2.Aq$, is found as *brochantite*.

Sulphate of copper cannot easily be separated by crystallisation from the sulphates of iron, zinc, and magnesium, because it forms double salts with them, which contain, like those sulphates, seven molecules of water, and are isomorphous with magnesium sulphate (unless the $CuSO_4$ is the predominant constituent, when the salts contain five molecules of water and are isomorphous with cupric sulphate). An instance of this is seen in the *black vitriol* obtained from the mother-liquor of the sulphate of copper at Mansfeld, and forming bluish-black crystals isomorphous with green vitriol, $FeSO_4.7H_2O$. The formula of black vitriol may be written $[CuMgFeMnCoNi]SO_4.7H_2O$, the six isomorphous metals being interchangeable without altering the general character of the salt.

Cupric arsenite, $CuHAsO_3$, has been noticed at page 240. It is a yellowish green powder, insoluble in water, but easily soluble in acids and alkalies. Its solution in potash has a dark blue colour, and deposits cuprous oxide when boiled, potassium arsenate being produced.

Cupric phosphide, Cu_3P_2, is obtained as a black precipitate by passing PH_3 into solution of cupric sulphate.

The basic *cupric phosphates* compose the minerals *tagilite* and *libethenite*.

The basic *cupric carbonates* have been noticed as forming the very beautiful minerals *blue malachite*, *azurite*, or *chessylite*, and *green malachite*.

Mineral green, $CuCO_3.Cu(OH)_2$, has the same composition as green malachite, and is prepared by mixing hot solutions of sodium carbonate and cupric sulphate. When boiled in the liquid, it is gradually converted into black oxide of copper. The green deposit formed on old copper by exposure to air has the same composition.

The blue precipitate produced in cupric solutions by alkaline carbonates in the cold is $CuCO_3.Cu(OH)_2.Aq$.

Cupric silicates are found in the minerals *dioptase*, or *emerald copper*, and *chrysocolla*, $CuH_2SiO_4.H_2O$.

267. CHLORIDES OF COPPER.—The chloride of copper (*cupric chloride*), $CuCl_2$, is produced by the direct union of its elements, when it forms a brown mass, which fuses easily, and is decomposed into chlorine and cuprous chloride, the latter being afterwards converted into vapour. When dissolved in water, it gives a solution which is green when concentrated, and becomes blue on dilution. The hydrated cupric chloride is readily prepared by dissolving the black oxide in hot hydrochloric acid, and allowing the solution to crystallise; it forms green needle-like crystals ($CuCl_2.2H_2O$) which become blue when dried *in vacuo* (Hartley). A solution of chloride of copper in alcohol burns with a splendid green flame, and the chloride imparts a similar colour to a gas flame.

Oxychloride of copper ($CuCl_2.3CuO.4H_2O$) is found at Atacama, in prismatic crystals, and is called *atacamite*. The paint *Brunswick green* has the same composition, and is made by moistening copper with solution of hydrochloric acid or sal-ammoniac, and exposing it to the air in order that it may absorb oxygen; $Cu_4 + 2HCl + 3H_2O + O_4 = CuCl_2.3CuO.4H_2O$. It is also made by boiling cupric sulphate with chloride of lime. The Brunswick green of the shops frequently consists of a mixture of Prussian blue, chromate of lead, and barium sulphate.

Subchloride of copper (*cuprous chloride*), Cu_2Cl_2 (= 2 vols.), is formed as a sublimate when copper is heated in HCl gas. It is also produced when fine copper turnings are shaken with strong hydrochloric acid in a bottle of air; $Cu_2 + 2HCl + O = Cu_2Cl_2 + H_2O$. The cuprous chloride dissolves in the excess of hydrochloric acid, forming a brown solution, from which water precipitates it *white*, for this is one of the few chlorides insoluble in water. When exposed to light, it assumes a purplish-grey tint. A copper plate dipped into a strong neutral solution of cupric chloride acquires a thin coating of cuprous chloride upon which photographs may be taken. Cuprous chloride may be prepared by dissolving 5 parts of black oxide of copper in hydrochloric acid, and boiling with 4 parts of fine copper turnings, the brown solution being afterwards precipitated by water. If the solution be moderately diluted and set aside, it deposits tetrahedral crystals of cuprous chloride. Ammonia (free from air) dissolves cuprous chloride to a colourless liquid, which becomes dark blue by contact with air, absorbing oxygen. The ammoniacal solution of cuprous chloride is employed as a test for acetylene (page 93), which gives a red precipitate with it. The solution may be preserved in a colourless state by keeping it in a well-stoppered bottle, quite full, with strips of clean copper. When copper, in a finely divided state, is boiled with solution of ammonium chloride, the solution deposits colourless crystals of the salt, $Cu_2Cl_2(NH_3)_2$. If the solution of this salt be exposed to the air, blue crystals are deposited, having the formula $Cu_2Cl_2.CuCl_2.4NH_3.H_2O$, and on further exposure, a compound of this last salt with ammonium chloride is deposited. The solution of cuprous chloride in hydrochloric acid is employed for absorbing carbonic oxide in the analysis of gaseous mixtures. When this solution is exposed to air it absorbs oxygen, and deposits cupric oxychloride. A strong solution of ammonium or sodium or potassium chloride readily dissolves the cuprous chloride, even in the cold, forming soluble double chlorides, such as $Cu_2Cl_2.4KCl$. The solution in potassium chloride does not absorb oxygen quite so easily as that in ammonium chloride.

Cuprous iodide, Cu_2I_2, is a very insoluble white precipitate formed when a mixture of cupric and ferrous sulphates is added to the solution of an iodide; $2CuSO_4 + 2FeSO_4 + 2KI = Cu_2I_2 + Fe_2(SO_4)_3 + K_2SO_4$. It is also precipitated, together with iodine, when cupric sulphate is added to an iodide; $2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$.

268. SULPHIDES OF COPPER.—Copper has a very marked attraction for sulphur, even at the ordinary temperature. A bright surface of copper soon becomes tarnished by contact with sulphur, and hydrosulphuric acid blackens the metal. Finely divided copper and sulphur combine slowly at the ordinary temperature, and when heated together, they combine with combustion. A thick copper wire burns easily in vapour of sulphur (page 191). Copper is even partly converted into sulphides when boiled

with sulphuric acid, as in the preparation of sulphurous acid gas. This great attraction of copper for sulphur is taken advantage of in the process of *kernel roasting* for extracting the copper from pyrites containing as little as 1 per cent. of the metal. The pyrites is roasted in large heaps (page 196) for several weeks, when a great part of the iron is converted into peroxide, and the copper remains combined with sulphur, forming a hard kernel in the centre of the lumps of ore. This kernel contains about 5 per cent. of copper, and can be smelted with economy. Children are employed to detach the kernel from the shell, which consists of ferric oxide mixed with a little cupric sulphate, which is washed out with water.

The *subsulphide of copper*, or *cuprous sulphide* (Cu_2S), has been mentioned among the ores of copper and among the furnace products in smelting, when it is sometimes obtained in octahedral crystals. It is formed when H_2S is passed over red-hot CuO, and when coal-gas is passed over red-hot CuS. It is not attacked by hydrochloric acid, but nitric acid dissolves it readily. *Copper pyrites* is believed to contain the copper in the form of cuprous sulphide, its true formula being $Cu_2S.Fe_2S_3$; for if the copper be present as cupric sulphide, CuS, the iron must be present as ferrous sulphide, and the mineral would have the formula $CuS.FeS$. Now, FeS is easily attacked by dilute sulphuric or hydrochloric acid, which is not the case with copper pyrites. Nitric acid, however, attacks it violently.

Sulphide of copper, or *cupric sulphide* (CuS), occurs in nature as *indigo copper* or *blue copper*, and may be obtained as a black precipitate by the action of hydrosulphuric acid upon solution of cupric sulphate. When this precipitate is boiled with sulphur and ammonium sulphide, it is dissolved in small quantity, and the solution on cooling deposits fine scarlet needles containing a higher sulphide of copper combined with sulphide of ammonium. When copper and sulphur are heated together in atomic proportions to a temperature below the boiling point of sulphur (440° C.), CuS is produced; but at a higher temperature, this is converted into Cu_2S. *Pentasulphide of copper* (CuS_5) is obtained by decomposing cupric sulphate with potassium pentasulphide; it forms a black precipitate distinguished from the other sulphides of copper by its solubility in potassium carbonate. The sulphides of copper, when exposed to air in the presence of water, are slowly oxidised and converted into cupric sulphate, which is dissolved by the water. It appears to be in this way that the *blue water* of the copper mines is formed.

Phosphide of copper, *cupric phosphide* (Cu_3P_2), obtained as a black powder by boiling solution of cupric sulphate with phosphorus, has been already mentioned as a convenient source of phosphine. Another phosphide, obtained by passing vapour of phosphorus over finely divided copper at a high temperature, is employed in Abel's composition for magneto-electric fuzes, in conjunction with cuprous sulphide and potassium chlorate. Phosphide of copper employed for toughening commercial copper is made by running melted copper into a conical iron crucible lined with loam, at the bottom of which are placed sticks of phosphorus which have been coated with copper by soaking them in cold solution of cupric sulphate.

Silicon may be made to unite with copper by strongly heating finely divided copper with silica and charcoal. A bronze-like mass is thus obtained containing about 5 per cent. of silicon. It is said to rival iron in ductility and tenacity, and fuses at about the same temperature as bronze.

LEAD.

$Pb'' = 206.5$ parts by weight.

269. Lead owes its usefulness in the metallic state chiefly to its softness and fusibility. The former quality allows it to be easily rolled into thin sheets and to be drawn into the form of tubes or pipes; it is indeed the softest of the metals in common use, and at the same time the least tenacious, so that it can only be drawn with difficulty into thin wire, and is then very easily broken. The ease with which it makes a dark streak upon paper shows how readily minute particles of the metal may be abraded. Its want of elasticity also recommends it for some special uses, as for deadening a shock or preventing a rebound.

In fusibility it surpasses all the other metals commonly employed in the metallic state, except tin, for it melts at 617° F. (325° C.), and this circumstance, taken in conjunction with its high specific gravity (11.4), particularly adapts it for the manufacture of shot and bullets. For one of its extensive uses, however, as a covering for roofs, it would be better suited if it were lighter and less fusible, for in case of fire in houses so roofed, the fall of the molten lead frequently aggravates the calamity. Its resistance to strong acids is turned to account in manufacturing chemistry.

With the exception, perhaps, of the ores of iron, none is more abundant in this country than the chief ore of lead, *galena*, a sulphide of lead (PbS). This ore might at the first glance be mistaken for the metal itself, from its high specific gravity and metallic lustre. It is found forming extensive veins in Cumberland, Derbyshire, and Cornwall, traversing a limestone rock in the two first counties, and a clay slate in the last. Spain also furnishes large supplies of this important ore.

Galena presents a beautiful crystalline appearance, being often found in large isolated cubes, which readily cleave or split up in directions parallel to their faces. Blende (sulphide of zinc) and copper pyrites (sulphide of copper and iron) are frequently found in the same vein with galena, and it is usually associated with quartz (silica), heavy spar (barium sulphate), or fluor spar (calcium fluoride). Considerable quantities of sulphide of silver are often present in galena, and in many specimens the sulphides of bismuth and antimony are found.

Though the sulphide is the most abundant natural combination of lead, it is by no means the only form in which this metal is found. The metal itself is occasionally met with, though in very small quantity, and the carbonate of lead ($PbCO_3$), *white lead ore* or *cerussite*, forms an important ore in the United States and in Spain. The sulphate of lead, *anglesite* ($PbSO_4$), is also found in Australia, and is largely imported into this country to be smelted.

270. The extraction of lead from galena is effected by taking advantage of the circumstance that, when a combination of a metal with oxygen is raised to a high temperature in contact with a sulphide of the same metal, the oxygen and sulphur unite, and the metal is liberated.

The ore, having been separated by mechanical treatment as far as possible from the foreign matters associated with it, is mixed with a small proportion of lime, and spread over the hearth of a reverberatory furnace (fig. 251), the sides of which are considerably inclined towards the centre, so as to form a hollow for the reception of the molten lead.

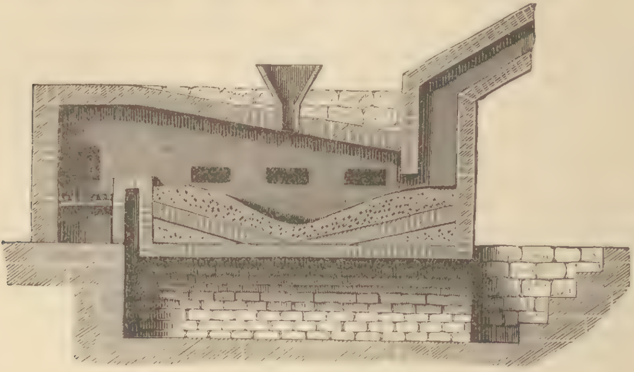

Fig. 251.—Furnace for smelting lead ores.

During the first stage of the smelting process, the object is to roast the ore with free access of air, exposing as large a surface as possible, on which account the temperature is kept below that at which galena fuses; indeed, during the first two hours no fuel is thrown into the grate, sufficient heat being radiated from the sides of the furnace, which have become red hot during the smelting of the previous charge of ore. The ore is stirred from time to time, to expose fresh surfaces to the action of the atmospheric oxygen.

The effect of this roasting is to convert a portion of the sulphide of lead (PbS) into sulphate of lead ($PbSO_4$), whilst another portion loses its sulphur, which is evolved as sulphurous acid gas (SO_2), and acquires oxygen in its stead, becoming converted into oxide of lead (PbO). A large proportion of the galena, however, remains unoxidised. When the roasting is sufficiently advanced, some fuel is thrown into the grate, some rich slags from previous smeltings are thrown on to the hearth, the damper is slightly raised, and the doors of the furnace are closed, so that the charge may be heated to the temperature at which the oxide and sulphate of lead act upon the unaltered sulphide, furnishing metallic lead, whilst the sulphur is expelled in the form of sulphurous acid gas; $PbS + 2PbO = Pb_3 + SO_2$ and $PbSO_4 + PbS = Pb_2 + 2SO_2$.

During this part of the operation the contents of the hearth are constantly raked up towards the fire-bridge, so as to facilitate the separation of the lead, and to cause it to run down into the hollow provided for its reception. It is also found that the separation of the lead from the slags is much assisted by occasionally throwing open the doors to chill the furnace. After about four hours the charge is reduced to a pretty fluid condition, the lead having accumulated at the bottom of the depressed portion of the hearth with the slag above it; this slag consists chiefly of the silicates of lime and oxide of lead, and would have contained a larger proportion of the latter if the lime had not been added as a flux at the commencement of the operation. In order still further to reduce the quantity of lead in the slag, a few more shovelfuls of lime are now thrown into the hearth, together with a little small coal, the latter serving to reduce to the metallic state the oxide of lead displaced by the lime from its combination with the silica. But since silicate of lime is far less fusible than silicate of lead, the effect of this addition of lime is to dry up the slags to a semi-solid mass, and it will now be seen that if the whole of the lime had been added at the commencement of the smelting, the diminished fusibility of the slag would have opposed an obstacle to the separation of the metallic lead.

During the last hour or so the temperature is very considerably raised, and at the expiration of about six hours, when the greater portion of the lead is thought to have separated, the slag is raked out through one of the doors of the furnace, and the melted metal allowed to run out through a tap-hole in front of the lowest portion of the hearth, into an iron basin, from which it is ladled into pig-moulds. The rich slags, together with the layer of subsulphide of lead (Pb_2S) which forms over the surface of the metal, are worked up again with a fresh charge of ore.

In the smelting of galena a very considerable quantity of lead is carried off in the form of vapour; and in order to condense this, the gases from the furnace are made to pass through flues, the aggregate length of which is sometimes three or four miles, before being allowed to escape up the chimney. When these flues are swept, many tons of lead are recovered in the forms of oxide and sulphide.

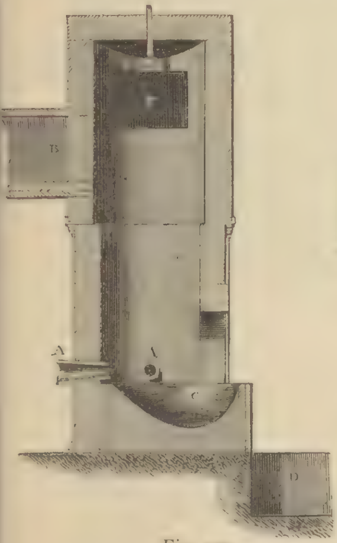

Fig. 252.

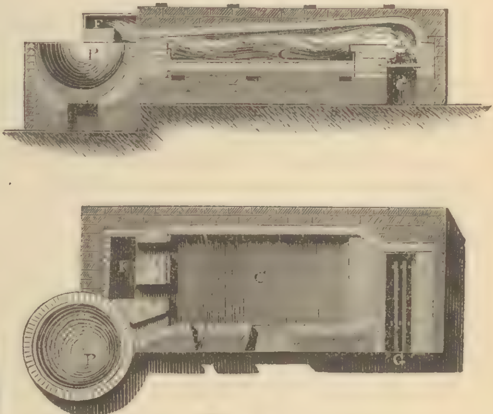

Fig. 253.

In the north of England the smelting of lead ores is now generally conducted in an *economico-furnace* (fig. 252), or small blast-furnace, instead of in the reverberatory furnace described above. Air is supplied to the furnace through three blast-pipes (A), and the ore and fuel being charged in at B, the lead runs into a cavity (C) at the bottom of the furnace, whilst the slag flows over into a reservoir (D) outside the furnace. The charge is sprinkled with water through the rose (E) fixed just above the opening into the chimney (F), to prevent it from being blown away by the current of air.

271. Some varieties of lead, particularly those smelted from Spanish ores, are known as *hard lead*, their hardness being chiefly due to the presence of antimony; and since this hardness interferes materially with some of the uses of the metal, such lead is generally subjected to an *improving* or *calcining* process, in which the impurities are oxidised and removed, together with a portion of the lead, in the dross.* To effect this, 6 or 8 tons of the hard lead are fused in an iron pot (P, fig. 253), and transferred to a shallow cast-iron pan (C) measuring about 10 feet by 5. In this pan, which is set in the hearth of a reverberatory furnace, and is about 8 inches deep nearest the grate and 9 inches at the other end, the lead is kept in fusion by the flame which traverses it from the grate G to the flue F, for a period varying with the degree of impurity, some specimens being found sufficiently soft after a single day's calcination, whilst others must be kept in a state of fusion for three or four weeks. The workman judges of the progress of the operation by a peculiar flaky crystalline appearance assumed by a small sample on cooling. When sufficiently purified, the metal is run off and cast into pigs.

At first sight, it is not intelligible how antimony should be removed from lead by calcination, since lead is the more easily oxidised metal. The result must be ascribed to the tendency of antimony to form antimonic oxide (Sb_2O_5), which combines with the oxide of lead. The dross (antimoniate of lead) formed in this process, when reduced to the metallic state, yields an alloy of lead with 30 or 40 per cent. of antimony, which is much used for casting type furniture for printers.

272. *Extraction of silver from lead.*—The lead extracted from galena often contains a sufficient quantity of silver to allow of its being profitably extracted. Previously to the year 1829, this was practicable only when the lead contained more than 11 ounces of silver per ton, for the only process then known for effecting the separation of the two metals was that of cupellation, which necessitates the conversion of the whole of the lead into oxide, which has then to be separated from the silver, and again reduced to the metallic state, thus consuming so large an amount of labour that a considerable yield of silver must be obtained to pay for it. By the simple and ingenious operation known as *Pattinson's desilverising process*, a very large amount of the lead can be at once separated in the metallic state with little expenditure of labour, thus leaving the remainder sufficiently rich in the more precious metal to defray the cost of the far more expensive process of cupellation, so that

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* The following analyses illustrate the composition of hard lead :—

	English.	Spanish.
Lead	99.27	95.81
Antimony	0.57	3.66
Copper	0.12	0.32
Iron	0.04	0.21
	100.00	100.00

3 or 4 ounces of silver per ton can be extracted with profit. Pattinson founded his process upon the observation that when lead containing a small proportion of silver is melted and allowed to cool, being constantly stirred, a considerable quantity of the lead separates in the form of crystals containing a very minute proportion of silver, almost the whole of this metal being left behind in the portion still remaining liquid.

Eight or ten cast-iron pots, set in brickwork, each capable of holding about 6 tons of lead, are placed in a row, with a fire-place underneath each of them (fig. 254). Suppose that there are ten pots numbered consecutively, that on the extreme left of the workman being No. 1, and that on his extreme right No. 10. About 6 tons of the lead containing silver are melted in pot No. 5, the metal skimmed, and the fire raked out from beneath so that the pot may gradually cool, its liquid contents being constantly agitated with a long iron stirrer. As the crystals of lead form, they are well drained in a perforated ladle (about 10 inches wide and 5 inches deep) and transferred to pot No. 4. When about $\frac{4}{5}$ths of the metals have thus been removed in the crystals, the portion still remaining liquid, which retains the silver, is ladled into pot No. 6, and the pot No. 5, which is now empty, is charged with fresh argentiferous lead to be treated in the same manner.

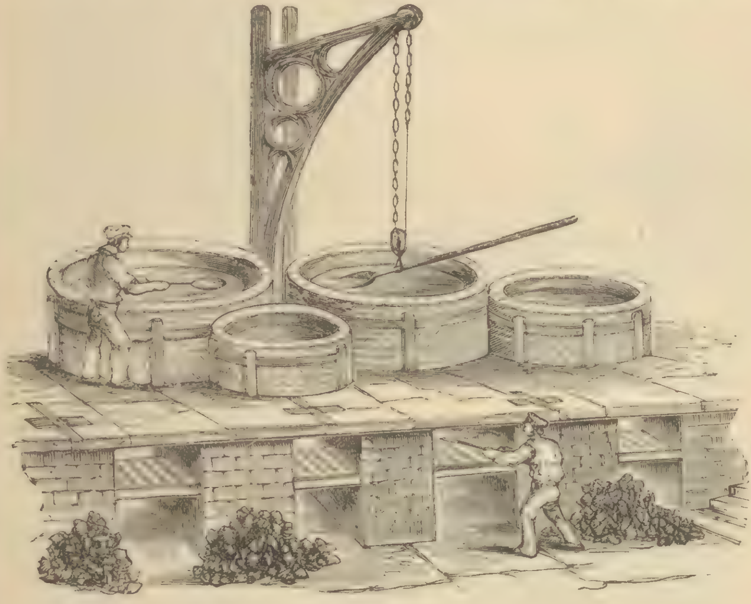

Fig. 254.—Pattinson's desilverising process.

When pots Nos. 4 and 6 have received, respectively, a sufficient quantity of the crystals of lead and of the liquid part rich in silver, their contents are subjected to a perfectly similar process, the crystals of lead being always passed to the left, and the rich argentiferous alloy to the right. As the final result of these operations, the pot No. 10, to the extreme right, becomes filled with a rich alloy of lead and silver, sometimes containing 300 ounces of silver to the ton, whilst pot No. 1. to the extreme left, contains lead in which there is not more than ½ ounce of silver to the ton. This lead is cast into pigs for the market. The ladle used in the above operation is kept hot by a small *temper pot* containing melted lead. A fulcrum is provided at the edge of each pot, for resting the ladle during the shaking of the crystals to drain off the liquid metal. Any copper present in the lead is also left with the silver in the liquid portion.

The employment of a jet of steam for stirring the bath of lead has much reduced the time and labour required in the above process. This also removes the copper as oxide, and the antimony is carried off in the steam.

273. In order to extract the silver from the rich alloy, it is subjected to a process of refining, or *cupellation*, which is founded upon the oxidation suffered by lead when heated in air, and upon the absence of any tendency on the part of silver to combine directly with oxygen.

The refinery or cupelling furnace (fig. 255), in which this operation is performed, is a reverberatory furnace, the hearth of which consists of a *cupel* (C), made by ramming moist powdered bone-ash mixed with a little wood-ash into an oval iron frame about 4 inches deep, and provided with four cross-bars at the bottom, each about 4 inches wide. When this frame has been well filled with bone-ash, part of it is scooped out, so as to leave the sides about 2 inches thick at the top and 3 inches at the bottom, the bone-ash being left about 1 inch thick above the iron cross-bars.

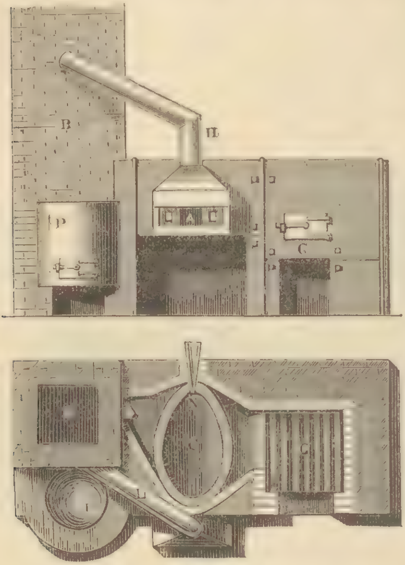

Fig. 255.—Cupellation furnace.

The cupel, which is about 4 feet long by 2½ feet wide, is fixed so that the flame from the grate (G) passes across it into the chimney (B), and at one end, the nozzle (N) of a blowing apparatus directs a blast of air over the surface of the contents of the cupel. The latter is carefully dried by a gradually increasing heat, and is then heated to redness; the alloy of lead and silver, having been previously melted in an iron pot (P) fixed by the side of the furnace, is ladled in through a gutter until the cupel is nearly filled with it; a film of oxide soon makes its appearance upon the surface of the lead, and is fused by the high temperature. When the blast is directed upon the surface, it blows off this film of oxide, and supplies the oxygen for the formation of another film upon the clean metallic surface thus exposed. A part of the oxide of lead or litharge thus formed is at first absorbed by the porous material of the cupel, but the chief part of it is forced by the blast through a channel cut for the purpose in the opposite end to that at which the blast enters, and is received, as it issues from A, in an iron vessel placed beneath the furnace. In proportion as the lead is in this manner removed from the cupel, fresh portions are supplied from the adjoining melting-pot, and the process is continued until about 5 tons of the alloy have been added.

The cupellation is not continued until the whole of the lead has been removed, but until only 2 or 3 cwts. of that metal are left in combination with the whole of the silver (say 1000 ounces) contained in the 5 tons of alloy. The metal is run through a hole made in the bottom of the cupel, which is then again stopped up so that a fresh charge may be introduced. The fumes of oxide of lead which are freely evolved during this process are carried off by a hood and chimney (H) situated opposite to the blast of air.

When three or four charges have been cupelled, so as to yield from 3000 to 5000 ounces of silver alloyed with 6 or 8 cwts. of lead, the removal of the latter metal is completed in another cupel, since some of the silver is carried off with the last portions of litharge. The appearances indicating the removal of the last portion of lead are very striking; the surface of the molten metal, which has been hitherto tarnished, becomes iridescent as the film of oxide of lead thins off, and afterwards resplendently bright, and when the cake of refined silver is allowed to cool, it throws up from its surface a variety of fantastic arborescent excrescences, caused by the escape of oxygen which has been mechanically absorbed by the fused silver, and is given off during solidification.

The litharge obtained from the cupelling furnaces is reduced to the metallic state by mixing it with small coal, and heating it in a furnace similar to that employed in smelting galena.

Another process for desilverising lead (*Parkes'*) consists in melting about 18 tons of the rich lead in a cast-iron pot, and stirring it with about 1 per cent. of zinc for twenty minutes; on standing, the zinc rises to the surface, bringing with it the silver and some lead, forming a solid crust, which is removed and distilled in a plumbago crucible to recover the zinc. The rich alloy of silver and lead remaining in the crucible is cupelled in the usual way. The desilverised lead is freed from zinc by the improving process (p. 388).

274. On the small scale, lead may easily be extracted from galena by mixing 300 grains with 450 grains of dried sodium carbonate and 20 grains of charcoal, introducing the mixture into a crucible, and placing in it two tenpenny nails, heads downwards. The crucible is covered and heated in a moderate fire for about half an hour. (A charcoal fire in the small furnace, fig. 130, page 116, will suffice.) The remainder of the nails is carefully removed from the liquid mass, which is then allowed to cool, the crucible broken, and the lead extracted and weighed. In this process the sulphur of the galena is removed, partly by the sodium of the carbonate and partly by the iron of the nails, the excess of sodium carbonate serving to flux any silica with which the galena may be mixed.

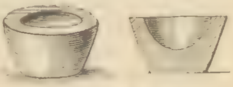
Fig. 256.

Or 300 grs. of galena may be mixed with 600 grs. of sodium carbonate and 200 grs. of nitre (which oxidises the sulphur), and fused for half an hour.

To ascertain if it contains silver, the button of lead is placed on a small bone-ash cupel (fig. 256), heated in a muffle (fig. 257), until the whole of the lead is oxidised and absorbed into the bone-ash of the cupel, leaving the minute globule of silver.

Small globules of lead may be conveniently cupelled on charcoal before the blowpipe, by pressing some bone-ash into a cavity scooped in the charcoal, placing the lead upon its surface, and exposing it to a good oxidising flame (page 109) as long as it decreases in size. If any copper be present, the bone-ash will show a green stain after cooling. Pure lead gives a yellow stain.

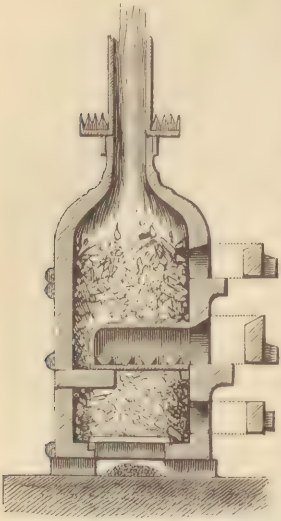

Fig. 257.

275. **Uses of lead.**—The employment of this metal for roofing, &c., has been already noticed. Its fusibility adapts it for casting type for printing, but it would be far too soft for this purpose; accordingly, *type-metal* consists of an alloy of 4 parts of lead with 1 of antimony. A similar alloy is used for the bullets contained in shrapnel shells, since bullets of soft lead would be liable to be jammed together, and would not scatter so well on the explosion of the shell. On the other hand, rifle bullets are made of very pure soft lead, in order that they may more easily take the grooves of the rifle.

Small shot are made of lead to which about 40 lbs. of arsenic per ton has been added. The arsenic dissolves in the lead, hardening it and causing it to form spherical drops when chilled. The fluid metal is poured through a sort of colander fixed at the top of a lofty tower (or at the mouth of a deserted coal shaft), and the minute drops into which it is thus divided are allowed to fall into a vessel of water, after having been chilled by the air in their descent. They are afterwards sorted, and polished in revolving barrels containing plumbago. If too little arsenic is employed, the shot are elongated or pyriform; and if the due proportion has been exceeded, their form is flattened or lenticular.

Composition tube used by plumbers is made of lead hardened by a little antimony.

Common solder is an alloy of equal weights of lead and tin, which is more fusible than either metal separately. Other alloys containing lead will be noticed in their proper places.

Leaden vessels are much used in manufacturing chemistry, on account of the resistance of this metal to the action of acids. Neither concentrated sulphuric,* hydrochloric, nitric, or hydrofluoric acid will act upon lead at the ordinary temperature. The best solvent for the metal is nitric acid of sp. gr. 1.2, since the nitrate of lead, being insoluble in an acid of greater strength, would be deposited upon the metal, which it would protect from further action.

Lead is easily corroded in situations where it is brought in contact with air highly charged with carbonic acid gas, when it absorbs oxygen, forming oxide of lead, which combines with carbonic acid gas and water to produce the basic carbonate of lead, $PbCO_3.Pb(OH)_2$. The lead of old coffins is often found converted into a white earthy-looking brittle mass of basic carbonate, with a very thin film of metallic lead inside it.

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* It has been found that pure lead is slowly acted on by sulphuric acid, hydrogen being evolved. The presence of a little antimony almost entirely prevents the action.

The basic carbonate is formed as a crystalline silky-looking precipitate when a piece of clean lead is left in distilled water for a few minutes.

When lead is exposed to the joint action of air and of the acetic acid contained in beer, wine, cider, &c., it becomes converted into acetate of lead or sugar of lead, which is very poisonous. Hence the accidents arising from the reprehensible practice of sweetening cider by keeping it in contact with lead, and from the accidental presence, in beer and wine bottles, of shot which have been employed in cleansing them. The action of water upon leaden cisterns has been already noticed. Contact with air and sea-water soon converts lead into oxide and chloride.

276. OXIDES OF LEAD.—Five compounds of lead with oxygen are known—Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2.

Lead suboxide, or *plumbous oxide*, Pb_2O, is obtained by heating lead oxalate; $2PbC_2O_4 = Pb_2O + CO + 3CO_2$. It is a black powder which is decomposed by acids, yielding plumbic salts and metallic lead.

The bright surface of lead soon tarnishes when exposed to the air, becoming coated with a dark film, which is believed to consist of suboxide of lead. In a very finely divided state, lead takes fire when thrown into the air, and is converted into oxide of lead.

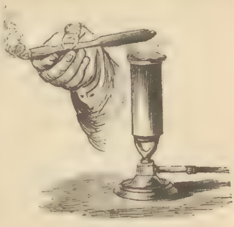
Fig. 258.

The *lead pyrophorus*, for exhibiting the spontaneous combustion of lead, is prepared by placing some lead tartrate in a glass tube closed at one end (fig. 258), drawing the tube out to a narrow neck near the open end, and holding it nearly horizontally, whilst the lead tartrate is heated with a gas or spirit flame as long as any fumes are evolved; the neck is then fused with a blowpipe flame and drawn off. Lead tartrate ($PbC_4H_4O_6$), when heated, leaves a mixture of metallic lead with charcoal, which prevents it from fusing into a compact mass. This mixture may be preserved unchanged in the tube for any length of time; but when the neck is broken off and the contents scattered into the air, they inflame at once, producing thick fumes of oxide of lead. Lead tartrate is prepared by adding solution of lead acetate to solution of tartaric acid constantly stirred, as long as a precipitate is formed. The precipitated lead tartrate is collected upon a filter, washed several times, and dried at a gentle heat.

Oxide or *protoxide of lead* (*plumbic oxide*) is sometimes found in nature, crystallised in rhombic octahedra, and is prepared on a large scale by heating lead in air. When the metal is only moderately heated, the oxide forms a yellow powder, which is known in commerce as *massicot*, but at a higher temperature the oxide melts, and on cooling forms a brownish scaly mass which is called *litharge* (*λίθος, stone; ἄργυρος, silver*), The litharge of commerce often has a red colour, caused by the presence of some red oxide of lead; from 1 to 3 per cent. of finely divided metallic lead may also sometimes be found in it. When heated to dull redness, litharge assumes a dark brown colour, and becomes yellow on cooling. At a bright red heat it fuses, and readily attacks clay crucibles, forming a fusible silicate of lead, and soon perforating the sides. When boiled with distilled water, litharge is dissolved in small quantity, yielding a solution which is decidedly alkaline, and becomes turbid when exposed to the air, absorbing carbonic acid gas, and depositing lead carbonate. The presence of a small quantity of saline matter in the water hinders the solution of the oxide, but organic matter, and especially sugar, favours it. Oxide of lead is a powerful base, and has a strong tendency to form basic salts. Hot solutions of potash and soda dissolve it readily, and deposit it in pink crystals on cooling.

Litharge, from its easy combination with silica at a high temperature, is much used in the manufacture of glass and in glazing earthenware. The assayer also employs it as a flux. A mixture of litharge with lime is sometimes applied to the hair, which it dyes of a purplish-black colour, due to the formation of lead sulphide from the sulphur existing in hair. *Dhil mastic*, used by builders in repairing stone, is a mixture of 1 part of massicot with 10 parts of brick-dust, and enough linseed oil to form a paste; it sets into a very hard mass, which is probably due partly to the formation of lead silicate, and partly to the *drying* of the linseed oil by oxidation favoured by the oxide of lead.

Lead sesquioxide, Pb_2O_3, is obtained as a yellow precipitate, by dissolving PbO in caustic soda and adding sodium hypochlorite. Cold HCl dissolves it to a yellow liquid, which slowly evolves chlorine. Nitric acid partly dissolves it, leaving a brown residue of PbO_2. Heat converts it into PbO.

Red lead, or *minium*, is prepared by heating massicot in air to about 600° F. (316° C.), when it absorbs oxygen, and becomes converted into red lead. The massicot for this purpose is prepared by heating lead in a reverberatory furnace to a temperature insufficient to fuse the oxide which is formed, and rejecting the first portions, which contain iron and other metals more easily oxidisable than lead (as cobalt), as well as the last, which contain copper and silver, less easily oxidised than lead. The intermediate product is ground to a fine powder and suspended in water; the coarser particles are thus separated from the finer, which are dried, and heated on iron trays placed in a reverberatory furnace, till the requisite colour has been obtained. Minium is largely used in the manufacture of glass, whence it is necessary that it should be free from the oxides of iron, copper, cobalt, &c., which would colour the glass. It is also employed as a common red mineral colour, and in the manufacture of lucifer matches.

When minium is treated with dilute nitric acid, lead nitrate, $Pb(NO_3)_2$, is obtained in solution, and peroxide of lead (PbO_2) is left as a brown powder, showing that minium is probably a compound of the oxide and peroxide of lead. The minium obtained by heating massicot in air till no further increase of weight is observed, has the composition $2PbO.PbO_2$ or Pb_3O_4, which would appear to represent pure minium; commercial minium, however, has more frequently a composition corresponding to $3PbO.PbO_2$, but when this is treated with potash, PbO is dissolved out, and $2PbO.PbO_2$ remains. Minium evolves oxygen at a red heat, becoming PbO; hence the necessity for keeping the temperature below 600° F. during its preparation. Hydrochloric acid, heated with minium, evolves chlorine, and leaves the white sparingly soluble $PbCl_2$. A mixture of dilute nitric acid and sugar, or some other oxidisable body, will dissolve minium entirely as $Pb(NO_3)_2$. Glacial acetic acid dissolves minium, without evolution of gas, to a colourless liquid which deposits PbO_2 when exposed to air or evaporated, or diluted.

Peroxide, or *dioxide*, or *puce oxide of lead* (*plumbic oxide*), is found in the mineral kingdom as *heavy lead ore*, forming black, lustrous, six-sided prisms. It may be prepared from red lead by boiling it, in fine powder, with nitric acid diluted with five measures of water, washing, and drying.

The dioxide of lead easily imparts oxygen to other substances; sulphur, mixed with six times its weight of PbO_2, may be ignited by friction; hence this oxide is a common ingredient in lucifer-match compositions. Its oxidising property is frequently turned to account in the laboratory; for example, in absorbing sulphur dioxide from gaseous mixtures by converting it into sulphate of lead; $PbO_2 + SO_2 = PbSO_4$. Dioxide of lead is not dissolved by dilute acids, and has no basic properties; indeed, it is sometimes called plumbic anhydride, for it acts upon potassium hydrate, yielding potassium plumbate ($K_2PbO_3.3H_2O$), which has been crystallised from an alkaline solution, but is decomposed by pure water. Lead dioxide evolves Cl from HCl when heated, and gives, at first, a brown solution which yields a brown precipitate with ammonia, but if the solution be boiled till all the Cl is expelled, it becomes colourless $PbCl_2$, and gives a white precipitate with ammonia. PbO is converted into PbO_2 by ozone and hydric peroxide.

Lead hydrate, or *hydroxide*, $Pb(HO)_2$, has not been obtained, but $Pb(HO)_2.PbO$ is formed as a white precipitate when air and water, free from CO_2, act upon lead. The same substance is precipitated by alkalies from solutions of lead salts. It becomes PbO when heated to 145° C. The compound $Pb(HO)_2.2PbO$ crystallises in octahedra from a solution of basic lead acetate mixed with ammonia.

Lead nitrate, $Pb(NO_3)_2$, crystallises in white octahedra from a solution of lead or its oxide in dilute nitric acid. It dissolves easily in water, but not in nitric acid or in alcohol. It is employed in dyeing and calico-printing. Several sparingly soluble *basic lead nitrates* are known. When digested with water and metallic lead, the nitrate gives a yellow solution which deposits yellow scaly crystals of the compound $Pb.OH.NO_3.Pb.OH.NO_2$.

277. *Lead carbonate*, $PbCO_3$, is found in nature, as *cerussite*, in transparent rhombic crystals isomorphous with arragonite. It may be precipitated by ammonium carbonate and lead acetate, or by passing CO_2 into a weak solution of lead acetate. Potassium and sodium carbonates precipitate basic lead carbonates.

White lead, or *ceruse*, is a basic carbonate, or combination of lead carbonate, $PbCO_3$, with variable proportions of lead hydrate, $Pb(OH)_2$. This substance is a constant product of the corrosive action of air and water upon the metal. Its formation is, of course, very much encouraged by the presence of organic matters in a state of decay, which evolve carbonic acid gas.

White lead is manufactured on the large scale by two processes, which depend, however, upon the same principle; this may be stated as follows: lead oxide, PbO, with acetic acid, $HC_2H_3O_2$, yields lead acetate, $Pb(C_2H_3O_2)_2$, conveniently written PbA_2. This combines with lead hydrate, forming basic lead acetate, $Pb\bar{A}_2 2Pb(HO)_2$. This is decomposed by carbonic acid gas, yielding basic lead carbonate and normal lead acetate; $PbA_2.2Pb(HO)_2 + CO_2 = PbCO_3.Pb(HO)_2 + PbA_2 + H_2O$. The normal acetate, in contact with lead, atmospheric oxygen, and water, is converted into the basic acetate; $PbA_2 + Pb_2 + O_2 + 2H_2O = PbA_2.2Pb(HO)_2$; this is again acted on by CO_2, and the process is continuous.

In the older of the two processes, commonly known as the Dutch process, metallic lead, in the form of square gratings cast from the purest lead, is placed over earthen pots containing a small quantity of common vinegar; a number of these pots being built up into heaps, together with alternate layers of dung or spent tan, the heaps are entirely covered up with the same material. The metal is thus exposed to conditions most favourable to its oxidation, viz., a very warm and moist atmosphere produced by the fermentation of the organic matters composing the heap, and the presence of a large quantity of acid vapour generated from the acetic acid of the vinegar. The lead is therefore soon converted into oxide, a portion of which unites with the acetic acid to form the tribasic acetate of lead, which is then decomposed by the carbonic acid gas, evolved from the fermenting dung or tan, yielding carbonate of lead, which combines with another portion of the oxide of lead and of water to form the white lead. The neutral acetate of lead left after the removal of the oxide of lead from the tribasic acetate, is now ready to take up an additional quantity of the oxide, and the process is thus continued until, in the course of a few weeks, the lead has become coated with a very thick crust of white lead; the heaps are then destroyed, the crust detached, washed to remove adhering acetate of lead, ground to a paste with water, and dried. Rolled lead is not so easily converted as cast lead.

The newer process is a more direct application of the same principle, for it consists in passing CO_2 into an intimate mixture of litharge with about 1 per cent. of lead acetate, and water. The CO_2 is obtained from brewers' fermenting tuns or from exhalations from the earth. Another process for making white lead is to grind together, for some hours, common salt, litharge, and water, and to pass CO_2 into the mixture until the liquid is neutral. Here, the formation of lead oxychloride instead of basic acetate, is probably the intermediate stage.

The usual composition of white lead is expressed by the formula $Pb(OH)_2.2PbCO_3$, though other basic carbonates of lead are often mixed with it.

White lead being very poisonous, its use by painters and others is generally attended with symptoms of lead poisoning, arising in many cases, probably, from neglecting to wash the hands before eating, the effect of lead being *cumulative*, so that minute doses may show their combined action after many days. Diluted sulphuric acid and solutions of the sulphates of magnesia and the alkalies are sometimes taken internally to counteract its effect, since the sulphate of lead is not poisonous.

All paints containing lead, and cards glazed with white lead, are blackened even by minute quantities of sulphuretted hydrogen, from the production of black sulphide of lead. If the blackened surface remain exposed to the light and air, it is bleached again, the sulphide of lead (PbS) being oxidised and converted into white sulphate of lead ($PbSO_4$), but this does not take place in the dark. A little sulphide of lead or powdered charcoal is sometimes mixed with commercial white lead to give it a bluish tint. White lead probably owes much of its value in oil-painting to the formation of a lead-salt with the fatty acid. Pure white lead is easily soluble in acetic and dilute nitric acids.

Lead sulphate, $PbSO_4$, is found naturally as *anglesite* or lead vitriol, in transparent rhombic prisms isomorphous with celestine and heavy spar, and is obtained as a heavy granular precipitate when sulphuric acid is added to a salt of lead. Stirring much promotes the precipitation.

Lead sulphate is very slightly soluble in water, and even less so in dilute sulphuric acid and in alcohol. It is soluble in strong sulphuric and hydrochloric acids, in sodium chloride and thiosulphate, and in ammonium acetate and tartrate. At a red heat it fuses without decomposition.

An *acid lead sulphate*, $PbH_2(SO_4)_2.Aq$, has been crystallised. The minerals *lanarkite* and *leadhillite* are compounds of sulphate and carbonate of lead, $PbSO_4(PbCO_3)_2.H_2O$. The chromates of lead have been already noticed.

Lead phosphate, $Pb_3(PO_4)_2$, and *arsenate*, associated with lead chloride and carbonate, are found in certain minerals.

278. *Lead chloride* ($PbCl_2$ = 2 vols.) forms the mineral termed *horn lead*. It is one of the few chlorides which are not readily soluble in water, and is precipitated when hydrochloric acid or a soluble chloride is added to a solution of lead. Boiling water dissolves about $\frac{1}{30}$th of its weight of lead chloride, and deposits it in beautiful shining white needles on cooling. Cold water dissolves about $\frac{1}{130}$th of its weight. It fuses easily and solidifies again to a horny mass, like fused silver chloride. It is converted into vapour at a high temperature. The specific gravity of this vapour at 1070° C. is 9.64 (theory requires 9.62). Lead chloride dissolves easily in strong HCl, and is precipitated by water. The solution of lead chloride in water is precipitated by adding strong HCl; hence, a dilute HCl solution, when cold, retains very little lead chloride. Like silver chloride, lead chloride is soluble in sodium thiosulphate.

The *lead oxychloride* ($PbCl_2.PbO$) is formed when lead chloride is heated in air, and occurs in nature as *matlockite*. *Pattinson's oxychloride*, $PbCl.OH$, is sometimes employed as a substitute for white lead in painting, being prepared for this purpose by decomposing finely powdered galena with concentrated hydrochloric acid ($PbS + 2HCl = PbCl_2 + H_2S$), washing the resulting lead chloride with cold water, dissolving it in hot water, and adding lime-water, which precipitates the oxychloride; $2PbCl_2 + Ca(OH)_2 = 2PbCl(OH) + CaCl_2$.

Turner's yellow (Paris yellow, patent yellow, mineral yellow) is another oxychloride of lead ($PbCl_2.7PbO$), prepared by heating a mixture of litharge and sal-ammoniac. It has a fine golden-yellow colour, is easily fused, and crystallises in octahedra on cooling. The mineral *mendipite* is an oxychloride of lead ($PbCl_2.2PbO$) which occurs in colourless prismatic crystals.

Lead tetrachloride, $PbCl_4$, probably exists in the brown solution of PbO_2 in cold HCl. It gives a brown precipitate of PbO_2 when diluted.

Lead chlorobromide ($PbBrCl$) has been found in crystals resembling lead chloride among the furnace-products in smelting lead carbonate ore.

Lead iodide (PbI_2) is obtained as a bright yellow precipitate on mixing solutions of nitrate or acetate of lead and potassium iodide. If it be allowed to settle, the liquid poured off, and the precipitate dissolved in boiling water (with one or two drops of hydrochloric acid), it forms a colourless solution, depositing golden scales as it cools.

Hydriodic acid converts metallic lead into PbI_2. Like mercuric iodide, it dissolves in the alkaline iodides. When heated, it becomes red, then black, fuses, and becomes a yellow crystalline mass on cooling.

279. SULPHIDES OF LEAD.—*Lead sulphide*, PbS, is found as galena, crystallised in dark grey lustrous cubes of sp. gr. 7.5. It fuses when

strongly heated, and vaporises in a current of gas, condensing in small crystals. When heated in air, it is converted into a mixture of PbO and $PbSO_4$. Strong HCl dissolves it when heated, evolving H_2S. Nitric acid dissolves it partly as lead nitrate, leaving some undissolved lead sulphate mixed with sulphur. Iron, at a high temperature, abstracts the sulphur from it. Lead sulphide is obtained as a black precipitate when hydrosulphuric acid or a soluble sulphide acts upon a solution containing lead, even in minute proportion.

A *persulphide of lead*, the composition of which has not been ascertained, is formed as a red precipitate when a solution of lead is mixed with a solution of an alkaline sulphide saturated with sulphur (or with solution of ammonium sulphide which has been kept till it has acquired a red colour). It is probably PbS_5.

Pb_2S and Pb_4S are obtained as semi-metallic masses by fusing lead sulphide with metallic lead.

Lead chlorosulphide ($3PbS.PbCl_2$) is obtained as a bright red precipitate when hydrosulphuric acid is added in small quantity to a solution of lead chloride in hydrochloric acid, or when freshly precipitated lead sulphide is heated with solution of lead chloride. It is decomposed by hot water.

Lead selenide (PbSe) occurs associated with the sulphide in some lead ores; it much resembles galena, and has the same crystalline form.

280. THALLIUM (Tl = 204 parts by weight).—The discovery of this metal in 1861 was one of the first results of the application of the new method of testing by observation of coloured lines in the spectrum of a flame, described at p. 273. Crookes was examining the spectrum obtained by holding in the flame of a Bunsen burner the deposit formed in the flues of a sulphuric acid chamber, in which pyrites was employed as the source of sulphur. A green line made its appearance in the spectrum, which a less acute and practised observer might have mistaken for one of the lines caused by barium (see fig. 227), with which it nearly coincides in position; but the line was much brighter than that produced by barium, and on instituting a searching analysis of the deposit, a metal was obtained which did not agree in properties with any hitherto described, and was named *thallium*, from θαλλός, *a young shoot*, in allusion to the vernal green colour of its spectrum line. It has since been detected in several mineral waters; but the pyrites obtained from Spain and Belgium appears to be its best source. From the flue-dust of the sulphuric acid chambers, the metal is extracted by a simple process, but large quantities must be operated on to obtain any considerable amount. The deposit is treated with boiling water, and the solution mixed with much strong hydrochloric acid, which precipitates the thallium as thallous chloride (TlCl); this is converted into acid thallous sulphate ($TlHSO_4$) by treatment with sulphuric acid, and this salt having been purified by recrystallisation, is decomposed by zinc, which precipitates metallic thallium in a spongy form, fusible into a compact mass in an atmosphere of coal gas.

In external characters thallium is very similar to lead; but it tarnishes much more rapidly when exposed to air, and the streak which it makes on paper soon becomes yellowish, being converted into thallous oxide, Tl_2O. If a tarnished piece of the metal be allowed to touch the tongue, a strongly alkaline taste is perceived, for the *thallous oxide* (Tl_2O) is very soluble in water, so that the tarnished metal becomes bright when immersed in water. If granulated thallium be exposed to moist air in a warm place, it absorbs oxygen and carbonic acid gas. On boiling with water and filtering, the alkaline solution deposits white needles of *thallous carbonate* (Tl_2CO_3), and afterwards yellow needles of *thallous hydrate* (TlOH). The ready solubility of the oxide seemed to require thallium to be classed among the alkali-metals, a view which was encouraged by the circumstance that its specific heat proved it to be monatomic like potassium and sodium. But thallium appears to be more nearly related to another monatomic metal, silver, by the sparing solubility of its chloride and the insolubility of its sulphide. The circumstance that it may be kept unaltered in water, and may be precipitated from its salts by zinc, at once removes it from the group of alkali-metals. The ready solubility of its oxide in water is only an exaggeration of the behaviour of the oxides of lead and silver, both of which dissolve slightly in water, yielding alkaline solutions. Moreover, its hydrate is far less stable than those of potassium and sodium, for it becomes Tl_2O when dried *in vacuo* over oil of vitriol. Diluted sulphuric acid acts upon thallium as upon zinc, evolving hydrogen. It is not much affected by diluted nitric acid in the cold; even on heating, the action is slow unless the acid is very weak. On cooling, the solution becomes filled with needles of *thallous nitrate.* Thallium burns in oxygen with a beautiful green flame, and the thallous chlorate has been recommended for the manufacture of green fires in place of barium chlorate (see page 165).

Thallous sulphate, Tl_2SO_4, is obtained by dissolving thallium in sulphuric acid and evaporating; the acid sulphate, $TlHSO_4$, first produced, being decomposed by further heating. Tl_2SO_4 is isomorphous with K_2SO_4, and it forms *thallous alum*, $TlAl(SO_4)_2.12Aq$, crystallising like potash-alum. *Thallous chloride*, $TlCl$, resembles lead chloride, being precipitated by adding HCl to a solution of a thallous salt, and being dissolved by boiling water from which it crystallises on cooling. *Thallous iodide*, TlI, is obtained as a yellow precipitate on adding potassium iodide to a thallous salt; when dried and heated, it fuses to a red liquid, which remains red after solidifying, and changes, after a time, to yellow. When spread on paper, the yellow iodide becomes red when heated, and remains red on cooling, but becomes yellow when rubbed with a hard body. *Thallous sulphide*, Tl_2S, is deposited as a brownish-black precipitate, on adding ammonium sulphide to a thallous salt. *Thallic oxide*, Tl_2O_3, is obtained by adding sodium hypochlorite to thallous chloride mixed with excess of sodium carbonate. It is a dark red substance, which evolves oxygen and leaves thallous oxide when heated. It is also a basic oxide, its sulphate having the composition $Tl_2(SO_4)_3.H_2O.6Aq$. *Thallic chloride*, $TlCl_3$, is formed by heating thallium in excess of chlorine; it is soluble and crystallisable.

Salts of thallium, like those of lead, are poisonous.

SILVER.

$Ag' = 108$ parts by weight.

281. In silver, we meet with the first metal hitherto considered which is not capable of undergoing oxidation in the air, and this, in conjunction with its beautiful appearance, occasions its manifold ornamental uses, which are much favoured also by the great malleability and ductility of this metal (in which it ranks only second to gold), for the former property enables it to be rolled out into thin plates or leaves, so that a small quantity of silver suffices to cover a large surface, whilst its ductility permits the wire-drawer to produce that extremely thin silver wire which is employed in the manufacture of silver lace.

Silver, although pretty widely diffused, is found in comparatively small quantity, and hence it bears a high value, which adapts it for a medium of currency.

As might be expected from its want of direct attraction for oxygen, silver is found frequently in the metallic or native state, crystallised in cubes or octahedra, which are sometimes aggregated together, as in the silver-mines of Potosi, into arborescent or *dendritic* forms; it generally contains copper and gold.* Silver is more frequently met with, however, in combination with sulphur, forming the sulphide of silver (Ag_2S), which is generally associated with large quantities of the sulphides of lead, antimony, and iron. The largest supplies of silver are obtained from the Mexican and Peruvian mines, but the quantity furnished by Saxony and Hungary is by no means insignificant. Silver chloride is found in considerable quantity in the spongy deposits of silica round the Great Salt Lake in Utah. The process by which silver is extracted from galena has been already described under the history of lead.

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* Flight found 23 per cent. of mercury in a specimen of native silver from Kongsberg. Other samples also proved to be amalgams.

The ores of copper (particularly the grey copper ore) often contain so much silver as to be worth working for that metal, in which case they are smelted in the usual way, when the copper obtained is found to contain the whole of the silver present in the ore. The silver is separated from the copper by taking advantage of the facility with which the former metal is dissolved by melted lead. The process of *liquation*, as it is termed, consists in fusing the argentiferous copper with about thrice its weight of lead, and casting the alloy thus obtained into cakes or discs, which are afterwards gradually heated upon a hearth (fig. 259), so contrived that the lead, which melts much more easily than the copper, may flow off in the liquid state, carrying with it, in the form of an alloy, the silver which was associated with the copper, leaving this last metal in porous masses, having the form of the original discs, upon the hearth. The lead and silver are separated by the process of cupellation (p. 390).

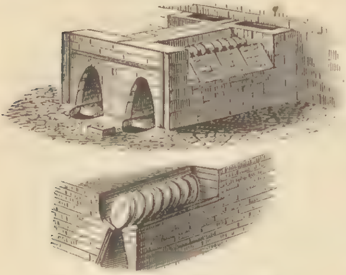

Fig. 259.—Liquation hearth.

When the extraction of the silver is the main object with which a particular ore is treated, the process of *amalgamation* is adopted, in which the silver is dissolved out by means of mercury. At Freiberg, the silver is extracted by this method from an ore which contains silver sulphide together with much iron pyrites and other metallic sulphides. The ore is mixed with a small proportion of common salt, and roasted in a reverberatory furnace, when the silver sulphide is converted into silver chloride. It is then ground to a very fine powder, which is agitated, in revolving casks, with water and metallic iron, when the latter appropriates the chlorine and reduces the silver to the metallic state. A quantity of mercury is then introduced into the casks, and the revolution continued for several hours; the mercury dissolves the silver, copper, and lead, and is run out of the barrels into stout linen strainers, which allow the excess of fluid mercury to pass through, but retain the soft solid amalgam containing the silver. In order to recover the silver, this amalgam is placed in iron trays arranged one above the other (fig. 260), and covered with an iron bell-shaped receiver standing over water. By heaping burning fuel round the upper part of this dome, its temperature is raised sufficiently to convert the mercury into vapour, which condenses again in the water, leaving the silver, together with the copper and lead, upon the iron trays. Finally, the silver is refined by fusing it with an additional quantity of lead and subjecting the alloy to cupel-

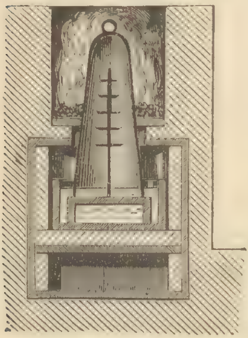

Fig. 260.

lation (p. 390), when the fused oxide of lead which is formed carries with it the copper, also in the form of oxide, leaving the silver in a state of purity.

Various methods have been devised to supersede the amalgamation process. For example, the ores have been roasted with common salt to convert the silver into chloride, which is dissolved out of the mass by means of a strong solution of common salt, from which the silver is afterwards precipitated in the metallic state by copper, or as silver iodide, by adding kelp liquor, the silver iodide being reduced by zinc, and the zinc iodide used to precipitate a fresh portion of silver. Sodium hyposulphite has also been employed to dissolve out the silver chloride, and the solution precipitated by sodium sulphide, the resulting silver sulphide being roasted to remove the sulphur and leave metallic silver.

Although silver is capable of resisting the oxidising action of the atmosphere, it is liable to considerable loss by wear and tear in consequence of its softness, and is therefore always hardened, for useful purposes, by the addition of a small proportion of copper. The *standard silver* employed for coinage and for most articles of silver plate in this country, contains, in 1000 parts, 925 of silver and 75 of copper, whilst that used in France contains 900 of silver and 100 of copper. English standard silver is said to have a *fineness* of 925, and French, of 900.

Standard silver, for coining and other purposes, is whitened by being heated in air and immersed in diluted sulphuric acid, which dissolves out the oxide of copper, leaving a superficial film of nearly pure silver. *Dead* or *frosted* silver is produced in this manner. *Oxidised* silver is covered with a thin film of sulphide by immersion in a solution obtained by boiling sulphur with potash.

The solder employed in working silver consists of 5 parts of silver, 2 of zinc, and 6 of brass.

Plated articles are manufactured from copper or one of its alloys, which has been united, by rolling, with a thin plate of silver, the adhesion of the latter being promoted by first washing the surface of the copper with a solution of silver nitrate, when a film of this metal is deposited upon its surface, the copper taking the place of the silver in the solution.

Electro-plating consists in covering the surface of baser metals with a coating of silver, by connecting them with the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving silver cyanide in potassium cyanide;* the current gradually decomposes the silver cyanide, and this metal is of course (see p. 11) deposited upon the object connected with the negative electrode, whilst the cyanogen liberated at the positive (copper or platinum) electrode is allowed to act upon a silver plate with which this is connected, so that the silvering solution is always maintained at the same strength, the quantity of silver dissolved at this electrode being precisely equal to that deposited at the opposite one.

Brass and copper are sometimes silvered by rubbing them with a mixture of 10 parts of silver chloride, with 1 of corrosive sublimate (mercuric chloride) and 100 of bitartrate of potash. The silver and mercury are both reduced to the metallic state by the baser metal, and an amalgam of silver is formed, which readily coats the surface. The acidity of the bitartrate of potash promotes the reduction. The surface to be silvered should always be cleansed from oxide by momentary immersion in nitric acid, and washed with water. For *dry silvering*, an amalgam of silver and mercury is applied to the clean surface, and the mercury is afterwards expelled by heat.

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* A solution of potassium cyanide in 10 parts of water, with 50 grains of silver chloride dissolved in each pint of the liquid, will answer the purpose.

Silvering upon glass is effected by means of certain organic substances which are capable of precipitating metallic silver from its solutions. Looking-glasses have been made by pouring upon the surface of plates of glass a solution containing silver tartrate and ammonium tartrate. On heating the glass plates to a certain temperature, the tartrate is reduced, and the metallic silver is deposited in a closely adhering film. Glass globes and vases are silvered internally by a process which is exactly similar in principle. The coating is rendered more adherent by sprinkling it with a weak solution of potassio-mercuric cyanide, which amalgamates the silver.

Small surfaces of glass for optical purposes may be silvered in the following manner: Dissolve one gramme of silver nitrate in 20 cubic centimetres of distilled water, and add weak ammonia carefully until the precipitate is almost entirely dissolved. Filter the solution and make it up to 100 cubic centimetres with distilled water. Then dissolve 2 grammes of silver nitrate in a little distilled water, and add it to a litre of boiling distilled water. Add 1.66 gramme of Rochelle salt (tartrate of potassium and sodium), and boil till the precipitated silver tartrate becomes grey; filter while hot.

Clean the glass to be silvered *very thoroughly* with nitric acid, distilled water, potash, distilled water, alcohol, distilled water; place it in a *clean* glass or porcelain vessel, with the side to be silvered uppermost. Mix equal measures of the two silver solutions (cold), and pour the mixture in so as to cover the glass, which will be silvered in about an hour. After washing, it may be allowed to dry, and varnished.—*Instruction in Physics in the Laboratory at South Kensington.*

Very good mirrors may be made by adding ammonia to weak silver nitrate till the precipitate just redissolves, then a little potash, then ammonia till the liquid is clear, and then a very little glycerin. If a watch-glass be floated on this liquid, and a gentle heat applied, a good mirror will be formed in a few minutes.

Pure silver is easily obtained from standard silver by dissolving it in nitric acid, with the aid of heat, diluting the solution with water, adding solution of common salt as long as it produces any fresh precipitate of silver chloride, washing the precipitate by decantation as long as the washings give a blue tinge with ammonia, and fusing the dried precipitate with half its weight of dried sodium carbonate in a brisk fire, when a button of silver will be found on breaking the crucible—

$$2AgCl + Na_2CO_3 = Ag_2 + 2NaCl + O + CO_2.$$

When fused in air, silver occludes oxygen, a portion of which it evolves during solidification, causing *sprouting* on the surface of the partly solidified metal, and sometimes projection of portions of the mass. After cooling, it still retains oxygen, which can only be expelled by heating to about 600° C. in a vacuum. This may amount to 0.025 per cent. by weight, and has to be taken into consideration in determining atomic weights in terms of silver.

282. Properties of silver.—The brilliant whiteness of silver distinguishes it from all other metals. It is lighter than lead, its specific gravity being 10.57; harder than gold, but not so hard as copper; more malleable and ductile than any other metal except gold, which it surpasses in tenacity. It fuses at a somewhat lower temperature than gold or copper (about 1900° F., 1037° C.), and is the best conductor of

heat and electricity. It may be distilled at a white heat. It is not oxidised by dry or moist air, either at the ordinary or at high temperatures, but is oxidised by ozone, and tarnished by air containing sulphuretted hydrogen, from the production of silver sulphide, which is easily removed by solution of potassium cyanide. Pure H_2S does not act upon silver. It is unaffected by dilute acids, with the exception of nitric; but hot concentrated sulphuric acid converts it into silver sulphate, and when boiled with strong hydrochloric acid, it dissolves to a slight extent in the form of silver chloride, which is precipitated on adding water. Strong hydriodic acid dissolves silver, evolving hydrogen; silver iodide is precipitated on addition of water. The potassium and sodium hydrates do not act on silver to the same extent as on platinum when fused with it; hence silver basins and crucibles are much used in the laboratory.

283. OXIDES OF SILVER.—There are three compounds of silver with oxygen—the suboxide, Ag_4O; the oxide Ag_2O; and the peroxide, probably Ag_2O_2, which is not known in the pure state. The oxide alone has any practical interest, as being the base of the salts of silver.

Silver oxide (Ag_2O) is obtained as a brown precipitate when solution of silver nitrate is decomposed by potash. It is prepared by dissolving half an ounce of silver nitrate in four ounces of water, and pouring it into a bottle containing three pints and a half of lime water. The oxide may be washed by decantation. It is a powerful base, slightly soluble in water, to which it imparts a weak alkaline reaction. A temperature of 250° C. decomposes it into its elements. It acts as a powerful oxidising agent. When moist freshly precipitated silver oxide is covered with a strong solution of ammonia, and allowed to stand for some hours, it becomes black, crystalline, and acquires dangerously explosive properties. The composition of this *fulminating silver* is not accurately known, but it is supposed to be a silver nitride, NAg_3, corresponding in composition to ammonia.

Silver nitrate ($AgNO_3$), or *lunar caustic* (silver being distinguished as *luna* by the alchemists), is procured by dissolving silver in nitric acid,* with the aid of a gentle heat, evaporating the solution to dryness, and heating the residue till it fuses, in order to expel the excess of acid. It fuses at 198° C. For use in surgery, the fused nitrate is poured into cylindrical moulds, so as to cast it into thin sticks; but for chemical purposes it is dissolved in water and crystallised, when it forms colourless square tables easily soluble in water and alcohol. The action of nitrate of silver as a caustic depends upon the facility with which it parts with oxygen, the silver being reduced to the metallic state, and the oxygen combining with the elements of the organic matter. This effect is very much promoted by exposure to sunlight, or diffused daylight. Pure silver nitrate is not changed by exposure to light, but if organic matter be present, a black deposit, containing finely divided silver, is produced. Thus, the solution of silver nitrate stains the fingers black when exposed to light, but the stain may be removed by potassium cyanide. If solution of silver nitrate be dropped upon paper, and exposed to light, black stains will be produced, and the paper corroded. Silver nitrate is a frequent constituent of marking-inks, since the deposit of metallic silver formed on exposure to light is not removable by washing. The linen is sometimes *mordanted* by applying a solution of sodium carbonate before the marking-ink, when the insoluble silver carbonate is precipitated in the fibre, and is more easily blackened than the nitrate, especially if a hot iron is applied. Marking-inks without preparation are made with silver nitrate containing an excess of ammonia, which appropriates the nitric acid, and hastens the blackening on exposure to light or heat. Hair-dyes often contain silver nitrate. The important use of this salt in photography has been noticed already (page 211).

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* For 3 ounces of silver, take 1¾ fluid ounce of strong nitric acid, and 5 fluid ounces of water.

Hydrogen slowly reduces silver nitrate, precipitating the metal.

In order to prepare silver nitrate from standard silver (containing copper), the metal is dissolved in moderately strong nitric acid, and the solution evaporated to dryness in a porcelain dish, when a blue residue containing the nitrates of silver and copper is obtained. The dish is now moderately heated until the residue has fused, and become uniformly black, the blue copper nitrate being decomposed and leaving black copper oxide, at a temperature which is insufficient to decompose the silver nitrate. To ascertain when all the copper nitrate is decomposed, a small sample is removed on the end of a glass rod, dissolved in water, filtered, and tested with ammonia, which will produce a blue colour if any copper nitrate is left. The residue is treated with hot water, the solution filtered from the copper oxide, and evaporated to crystallisation.

Silver nitrate forms crystalline double salts with one molecule of potassium or ammonium nitrate.

Silver ammonio-nitrate, $AgNO_3.2NH_3$, may be crystallised from a strong solution of silver nitrate saturated with ammonia.

Silver nitrite, $AgNO_2$, is obtained as a white precipitate from potassium nitrite and silver nitrate. It is soluble in hot water and crystallises in prisms. By long boiling with water, it is decomposed-

$$2AgNO_2 = AgNO_3 + Ag + NO.$$

Silver hyponitrite, $AgNO$, forms a yellow precipitate resembling Ag_3PO_4 (see p. 144).

Silver carbonate, Ag_2CO_3, is obtained in transparent yellow crystals when moist silver oxide is acted on by carbonic acid. It dissolves in solution of carbonic acid, like $CaCO_3$, and is deposited in crystals when the solution is exposed to the air. It is feebly alkaline to moist test-paper. It bears heating to nearly the boiling point of oil, and fuses just before decomposition. Silver carbonate forms a yellowish white precipitate when silver nitrate is decomposed by an alkaline carbonate.

284. *Silver chloride*, or *argentic chloride* ($AgCl$), is an important compound, as being the form into which silver is commonly converted in extracting it from its ores, and in separating it from other metals. It separates as a white curdy precipitate, when solution of hydrochloric acid or a chloride is mixed with a solution containing silver. The precipitate is brilliantly white at first, but soon becomes violet, and eventually black, if exposed to daylight, or more rapidly in sunlight, the chloride of silver being reduced to subchloride (Ag_2Cl), with separation of chlorine (see page 211). The blackening takes place more rapidly in the presence of an excess of silver nitrate or of organic matter, upon which the liberated chlorine is capable of acting. The silver chloride formed by suspending silver leaf in a bottle of chlorine gas, is not blackened by light. If the white silver chloride be dried in the dark, and heated in a crucible, it fuses at 451° C., to a

brownish liquid, which solidifies, on cooling, to a transparent, nearly colourless mass, much resembling horn in external characters (*horn silver*); a strong heat converts it into vapour, but does not decompose it. If fused silver chloride be covered with hydrochloric acid, and a piece of zinc placed upon it, it will be found entirely reduced, after a few hours, to a cake of metallic silver; the first portion of silver having been reduced in contact with the zinc, and the remainder by the galvanic action set up by the contact of the two metals beneath the liquid. Fusion with sodium carbonate reduces silver chloride—

$$2AgCl + Na_2CO_3 = Ag_2 + 2NaCl + CO_2 + O.$$

Silver chloride is slightly soluble in strong HCl, and in strong solutions of alkaline chlorides. Potassium cyanide dissolves it readily, and the solution is used in electro-plating. Ammonia readily dissolves silver chloride, and the solution deposits colourless crystals of the chloride when evaporated. If the ammonia be very strong, the solution deposits a crystalline compound of silver chloride with ammonia, $2AgCl.3NH_3$. The absorption of ammoniacal gas by silver chloride has been noticed at page 127, and the photographic application of the chloride at page 211.

Recovery of silver from old photographic baths.—One of the simplest methods of effecting this consists in mixing the liquid with solution of common salt as long as it causes a fresh precipitate of silver chloride, which is allowed to subside, washed once or twice by decantation, mixed with a little sulphuric acid, a lump of zinc (spelter) placed in it, and left for a day or two to reduce the silver to the metallic state. The zinc is then taken out, and the metallic silver well washed by decantation, first with dilute sulphuric acid, to remove zinc, and afterwards with water, till the washings are quite tasteless. It may either be reconverted into nitrate by dissolving in nitric acid (p. 403), or fused in an earthen crucible with a little borax.

From the fixing solutions containing sodium hyposulphite, the silver cannot be precipitated by salt, because the silver chloride is soluble in the hyposulphite. A piece of sheet copper left in this for a day or two will precipitate the silver at once in the metallic state.

Subchloride of silver, or *argentous chloride* (Ag_2Cl), has been obtained by the action of ferric chloride upon metallic silver; $Ag_4 + Fe_2Cl_6 = 2Ag_2Cl + 2FeCl_2$. It is black, and insoluble in nitric acid. Ammonia decomposes it, dissolving out silver chloride, and leaving metallic silver.

Another subchloride of silver, Ag_4Cl_3, has been obtained as a black powder by the action of hydrochloric acid upon the argentous citrate prepared by reducing argentic citrate with hydrogen.

Silver bromide (AgBr) is a rare Chilian mineral, *bromargyrite*. Associated with silver chloride, it forms the mineral *embolite*. It much resembles the chloride, but is somewhat less easily dissolved by ammonia. Dry silver bromide does not absorb ammonia gas. When heated to 700° C. in HCl, silver bromide is converted into the chloride, but, at the ordinary temperature, HBr converts silver chloride into bromide.

Silver iodide (AgI) is also found in the mineral kingdom. It is worthy of remark that silver decomposes hydriodic acid much more easily than hydrochloric acid, forming silver iodide, and evolving hydrogen. The silver iodide dissolves in hot hydriodic acid, and the solution deposits crystals of AgI.HI, which are decomposed in the air. If the hot solution be left in contact with silver, prisms of AgI are deposited. By adding silver nitrate to potassium iodide, the silver iodide is obtained as a yellow precipitate, which, unlike the chloride, does not dissolve in ammonia, but is bleached, forming $2AgI.NH_3$, which is also produced when dry silver iodide absorbs ammonia. Silver iodide is remarkable for contracting when heated between the temperatures of – 10° C. and 70° C. It fuses easily, like the chloride. When heated to 700° C. in HCl, it is converted into AgCl, but, at ordinary temperatures, both AgCl and AgBr are converted by HI into AgI. Light has no visible effect on pure AgI; but if the AgI which has been exposed to light be acted on by $AgNO_3$ and a reducing agent, such as pyrogallol, metallic silver is precipitated upon its surface, so that only those portions of the silver iodide which have been exposed to light will be *developed* or rendered visible, and if the unaltered iodide be dissolved away by potassium cyanide, a permanent *negative* picture will be left. Silver iodide dissolves in a boiling saturated solution of silver nitrate, and the solution, on cooling, deposits crystals having the composition $AgI.AgNO_3$, which are far more sensitive to the action of light than silver iodide itself, a circumstance which is taken advantage of by photographers. The crystals are decomposed by water, with separation of silver iodide.

Silver fluoride, AgF, is deliquescent and very soluble in water, forming crystals which may contain one or two molecules of water. It fuses to a horny mass, like AgCl, but is reduced to the metallic state when heated in moist air. Ammonia also reduces it to the metallic state when heated. Fused AgF conducts the electric current without undergoing decomposition.

Silver sulphide (Ag_2S) is found as *silver glance*, which may be regarded as the chief ore of silver; it has a metallic lustre, and is sometimes found in cubical or octahedral crystals. The minerals known as *rosiclers* or *red silver ores* contain sulphide of silver combined with the sulphides of arsenic and antimony. The black precipitate obtained by the action of hydrosulphuric acid upon a solution of silver is silver sulphide. It may also be formed by heating silver with sulphur in a covered crucible. Silver sulphide is remarkable for being soft and malleable, so that medals may even be struck from it. It is not dissolved by diluted sulphuric or hydrochloric acid, but nitric acid readily dissolves it. Metallic silver dissolves silver sulphide when fused with it, and becomes brittle even when containing only 1 per cent. of the sulphide. Roasting in air converts Ag_2S into Ag_2SO_4.

Silver sulphate, Ag_2SO_4, forms a crystalline precipitate when a strong solution of silver nitrate is stirred with dilute sulphuric acid. It requires 200 parts of cold water for solution. When moderately heated, it fuses without decomposition.

Hydro-argentic sulphate, $AgHSO_4$, has been crystallised.

Silver sulphite, Ag_2SO_3, forms a white precipitate when sulphurous acid is added to silver nitrate. Boiling with water reduces it to metallic silver; $Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4$.

Silver orthophosphate, Ag_3PO_4, forms a yellow precipitate when sodium phosphate is added to silver nitrate—

$$Na_2HPO_4 + 3AgNO_3 = 2NaNO_3 + HNO_3 + Ag_3PO_4.$$

It is soluble in nitric acid and in ammonia, and is thus distinguished from silver iodide.

Silver arsenite, Ag_3AsO_3, is obtained as a yellow precipitate when ammonia is cautiously added to a mixture of silver nitrate and arsenious acid; it is soluble in nitric acid and in ammonia.

Silver arsenate, Ag_3AsO_4, forms a red precipitate, soluble in nitric acid and in ammonia, when silver nitrate is added to arsenic acid.

Silver sulpharsenite, Ag_3AsS_3, is found as *light red silver ore.*

Silver sulphantimonate, Ag_3SbS_3, is *dark red silver ore.*

MERCURY.

Hg'' = 200 parts by weight[*] = 2 vols.

285. Mercury (*quicksilver*) is conspicuous among metals by its fluidity, and among liquids by its not wetting or adhering to most solids, such as glass, a property of great value in making philosophical instruments. It is the only metal which is liquid at the ordinary temperature, and since it requires a temperature of – 39° F. to solidify it, this metal is particularly adapted for the construction of thermometers and barometers. Its high boiling point (662° F., 350° C.) also recommends it for the former purpose, as its high specific gravity (13.54) does for the latter, a column of about 30 inches in height being able to counterpoise a column of the atmosphere having the same sectional area. The symbol for mercury (Hg) is derived from the Latin name for this element, *hydrargyrum* (*ὕδωρ, water*, referring to its fluidity, *ἄργυρος, silver*).

Mercury is not met with in this country, but is obtained from Idria (Austria), Almaden (Spain), China, and New Almaden (California). It occurs in these mines partly in the metallic state, diffused in minute globules or collected in cavities, but chiefly in the state of cinnabar, which is mercuric sulphide (HgS).

The metal is extracted from the sulphide at Idria by roasting the ore in a kiln (fig. 261), which is connected with an extensive series of condensing chambers built of brickwork. The sulphur is converted, by the air in the kiln, into sulphurous acid gas, whilst the mercury passes off in vapour and condenses in the chambers.

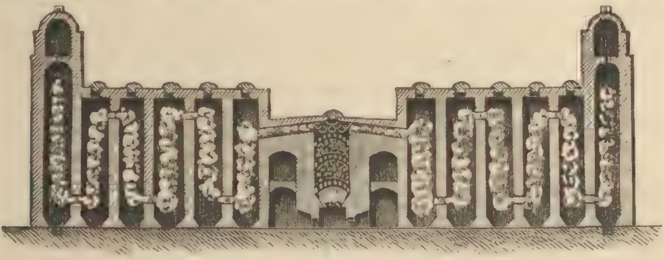

Fig. 261.—Extraction of mercury at Idria.

At Almaden, the extraction is conducted upon the same principle, but the condensation of the mercury is effected in earthen receivers (called *aludels*) opening into each other, and delivering the mercury into a gutter which conveys it to the receptacles.

The cinnabar is placed upon the arch (A, fig. 262) of brickwork, in which there are several openings for the passage of the flame of the wood fire kindled at B; this flame ignites the sulphide of mercury, which burns in the air passing up from below, forming sulphurous acid gas and vapour of mercury ($HgS + O_2 = Hg + SO_2$), which escape through the flue (F) into the aludels (C), where the chief part of the mercury condenses and runs down into the gutter (G). The sulphurous acid gas escapes through the flue (H), and any mercury which may have escaped condensation is collected in the trough (D), the gas finally passing out through the chimney (E), which provides for the requisite draught.

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[*] The vapour of mercury is only 100 times as heavy as hydrogen, which would indicate 100 as the atomic weight of mercury, but the specific heat of mercury when multiplied by 100 would give an atomic heat only half that of most other metals.

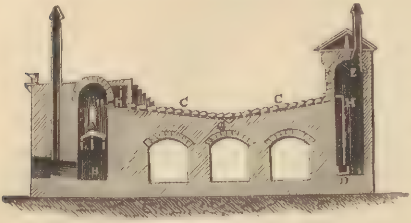

Fig. 262.

In the Palatinate, the cinnabar is distilled in cast-iron retorts with lime, when the sulphur is left in the residue as calcium sulphide and sulphate, whilst the mercury distils over—

$$4HgS + 4CaO = 3CaS + CaSO_4 + Hg_4.$$

The mercury found in commerce is never perfectly pure, as may be shown by scattering a little upon a clean glass plate, when it *tails* or leaves a track upon the glass, which is not the case with pure mercury. Its chief impurity is lead, which may be removed by exposing it in a thin layer to the action of nitric acid diluted with two measures of water, which should cover its surface, and be allowed to remain in contact with it for a day or two, with occasional stirring. The lead is far more easily oxidised and dissolved than the mercury, though a little of this also passes into solution. The mercury is afterwards well washed with water and dried, first with blotting-paper, and then by a gentle heat. Mercury is easily freed from mechanical impurities by filtering it through a cone of paper, round the apex of which a few pin-holes have been made. Zinc, tin, and bismuth are sometimes present in the mercury of commerce, and may be partly removed, as oxides, by shaking the mercury in a large bottle with a little powdered loaf-sugar for a few minutes, and straining through perforated paper. The sugar appears to act mechanically by dividing the mercury.

286. In its chemical properties, mercury much resembles silver, being unaffected by ordinary air, and tarnished by air containing H_2S. In course of time, however, it becomes oxidised, as may be seen in old instruments containing mercury and air; and it is slowly oxidised when heated in air, which is not the case with silver. It also appears to undergo a partial oxidation when reduced to a fine state of division, as in those medicinal preparations of the metal which are made by triturating it with various substances which have no chemical action upon it, until globules of the metal are no longer visible. *Blue pill* and *grey powder*, or *hydrargyrum cum cretâ*, afford examples of this, and probably owe much of their medicinal activity to the presence of one of the oxides of mercury.

Nitric acid dissolves mercury, and converts it into two nitrates—mercurous, $HgNO_3$, corresponding to $AgNO_3$, and mercuric, $Hg(NO_3)_2$. Hot concentrated sulphuric acid also converts it into mercurous (Hg_2SO_4) and mercuric ($HgSO_4$) sulphate. Mercury is precipitated from solutions of its salts by reducing agents, stannous chloride, for example, in what looks like a dark grey powder; but if this be boiled in the liquid, the minute globules of which it is composed gradually unite into fluid mercury. Conversely, if mercury be diligently triturated with chalk or grease, it may be divided into extremely minute globules which behave like a powder.

287. USES OF MERCURY.—One of the chief uses to which mercury is devoted is the *silvering of looking-glasses*, which is effected by means of an amalgam of tin in the following manner :—A sheet of tin-foil of the same size as the glass to be silvered is laid perfectly level upon a table, and rubbed over with metallic mercury, a thin layer of which is afterwards poured upon it. The glass is then carefully slid on to the table, so that its edge may carry before it part of the superfluous mercury with the impurities upon its surface ; heavy weights are laid upon the glass so as to squeeze out the excess of mercury, and in a few days the combination of tin and mercury is found to have adhered firmly to the glass ; this coating usually contains about 1 part of mercury and 4 parts of tin. In this and all other arts in which mercury is used (such as barometer-making) much suffering is experienced by the operatives, from the poisonous action of the mercury.

The readiness with which mercury unites with most other metals to form *amalgams* is one of its most striking properties, and is turned to account for the extraction of silver and gold from their ores. The attraction of the latter metal for mercury is seen in the readiness with which it becomes coated with a silvery layer of mercury, whenever it is brought in contact with that metal, and if a piece of gold leaf be suspended at a little distance above the surface of mercury, it will be found, after a time, silvered by the vapour of the metal which rises slowly even at the ordinary temperature. From the surface of rings which have been accidentally whitened by mercury, it may be removed by a moderate heat, or by warm dilute nitric acid, but the gold will afterwards require burnishing.

Zinc plates are *amalgamated*, as it is termed, for use in the galvanic battery, by rubbing the liquid metal over them under the surface of dilute sulphuric acid, which removes the coating of oxide from the surface of the zinc. The amalgam of zinc is not acted on by the diluted sulphuric acid used in the battery (see page 10) until the *circuit* is completed, so that no zinc is wasted when the battery is not in use. An amalgam of 6 parts of mercury with 1 part of zinc and 1 of tin is used to promote the action of frictional electrical machines.

The addition of a little amalgam of sodium to metallic mercury gives it the power of adhering much more readily to other metals, even to iron. Such an addition has been recommended in all cases where metallic surfaces have to be amalgamated, and especially in the extraction of silver and gold from their ores by means of mercury. *Gold amalgam* and *cadmium amalgam* are used by dentists. *Sodium amalgam*, in contact with water, forms a convenient source of *nascent* (atomic) hydrogen.

Iron and platinum are the only metals in ordinary use which can be employed in contact with mercury without being corroded by it. Mercury, however, adheres to platinum.

The following definite compounds of mercury with other metals have been obtained by combining them with excess of mercury, and squeezing out the fluid metal by hydraulic pressure, amounting to 60 tons upon the inch :—

Amalgam of	lead	Pb_2Hg	Amalgam of zinc	Zn_2Hg
,,	silver	$AgHg$	,, copper	$CuHg$
,,	iron	$FeHg$*	,, platinum	$PtHg_2$

* Hg_3Fe_2 has been obtained by the action of finely divided iron on sodium amalgam in presence of water.

The amalgam of silver (AgHg) has been found in nature, in dodecahedral crystals.

A very beautiful crystallisation of the amalgam of silver (*Arbor Dianæ*) may be obtained in long prisms having the composition Ag_2Hg_3, by dissolving 400 grains of silver nitrate in 40 measured ounces of water, adding 160 minims of concentrated nitric acid, and 1840 grains of mercury; in the course of a day or two crystals of 2 or 3 inches in length will be deposited.

288. OXIDES OF MERCURY.—Two oxides of mercury are known—the suboxide, Hg_2O, and the oxide, HgO; both combine with acids to form salts.

Suboxide of mercury, black oxide, or *mercurous oxide*, Hg_2O, is obtained by decomposing calomel with solution of potash, and washing with water; $Hg_2Cl_2 + 2KHO = Hg_2O + 2KCl + H_2O$. It is very easily decomposed, by exposure to light or to a gentle heat, into mercuric oxide and metallic mercury.

Red oxide of mercury, or *mercuric oxide* (HgO), is formed upon the surface of mercury, when heated for some time to its boiling point in contact with air. The oxide is black while hot, but becomes red on cooling. It is used, under the name of *red precipitate*, in ointments, and is prepared for this purpose by dissolving mercury in nitric acid, evaporating the solution to dryness, triturating the mercuric nitrate with an equal weight of mercury, and heating as long as acid fumes are evolved; $Hg(NO_3)_2 + Hg_2 = 3HgO + N_2O_3$. The name *nitric oxide of mercury* refers to this process. It is thus obtained, after cooling, as a brilliant red crystalline powder, which becomes nearly black when heated, and is resolved into its elements at a red heat. It dissolves slightly in water, and the solution has a very feeble alkaline reaction. A bright yellow modification of the oxide is precipitated when a solution of corrosive sublimate is decomposed by potash ($HgCl_2 + 2KHO = HgO + 2KCl + H_2O$); the yellow variety is chemically more active than the red.

When mercuric oxide is acted on by strong ammonia, it becomes converted into a yellowish-white powder which possesses the properties of a strong base, absorbing carbonic acid eagerly from the air, and combining readily with other acids. It is easily decomposed by exposure to light, and, if rubbed in a mortar when dry, is decomposed with slight detonations, a property in which it feebly resembles fulminating silver (p. 403). The composition of this substance is represented by the formula $NHg''_2.OH.2Aq$. When exposed *in vacuo* over oil of vitriol, it loses 2Aq, becoming $NHg''_2.OH$, or dimercurammonium hydrate, which is a brown explosive base.[*]

By passing ammonia gas over the yellow oxide of mercury as long as it is absorbed, and heating the compound to about 260° F. in a current of ammonia as long as any water is evolved, a brown explosive powder is obtained which is believed to be a *nitride of mercury*, $N_2Hg''_3$, representing a double molecule of ammonia in which the hydrogen has been displaced by mercury. It yields salts of ammonium when decomposed by acids.

289. The salts formed by the oxides of mercury with the oxygen-acids are not of great practical importance. *Protonitrate of mercury*, or *mercurous nitrate*, is obtained when mercury is dissolved in cold nitric acid diluted with 5 volumes of water; it may be procured in crystals having the composition $Hg_2(NO_3)_2.2Aq$. The prismatic crystals which are sometimes sold as protonitrate of mercury consist of a basic nitrate, $Hg_4(NO_3)_3OH$, prepared by acting with diluted nitric acid upon mercury in excess. When this salt is powdered in a mortar with a little common salt, it becomes black from the separation of mercurous oxide—

$$2Hg_4(NO_3)_3OH + 6NaCl = 6NaNO_3 + 3Hg_2Cl_2 + Hg_2O + H_2O;$$

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[*] It has been stated that by heating it for some time in a current of dry ammonia, the whole of the oxygen may be expelled as water, leaving the oxide of mercurammonium, $(NHg''_2)_2O$, which is very explosive, and combines with water to form a hydrate which produces salts with the acids.

but the normal nitrate is not blackened ($Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 + 2NaNO_3$). Mercurous nitrate is soluble in a little hot water, but much water decomposes it into nitric acid and a basic nitrate; $Hg_2(NO_3)_2 + H_2O = Hg_2NO_3.OH + HNO_3$.

Nitrate of mercury, or *mercuric nitrate*, is formed when mercury is dissolved with an excess of strong nitric acid, and the solution boiled until it is no longer precipitated by NaCl. It may be obtained in crystals of the formula $2Hg(NO_3)_2.Aq$. Water decomposes it, precipitating a yellow basic nitrate, which leaves mercuric oxide when long washed with water. Mercuric nitrate stains the skin red. When nitric acid is heated with an excess of mercuric oxide, the solution, on cooling, deposits crystals of a *basic mercuric nitrate*, $Hg_2(NO_3)_3.OH.Aq$.

Mercurous sulphate (Hg_2SO_4) is precipitated as a white crystalline powder when dilute sulphuric acid is added to a solution of mercurous nitrate.

Mercuric sulphate ($HgSO_4$) is obtained by heating 2 parts by weight of mercury with 3 parts of oil of vitriol, and evaporating to dryness. Mercurous sulphate is first produced, and is oxidised by the excess of sulphuric acid. It forms a white crystalline powder, which becomes brown-yellow when heated, and white again on cooling. It is decomposed by water into a soluble acid sulphate, and an insoluble yellow basic sulphate of mercury, $HgSO_4.2HgO$, known as *turbith* or *turpeth* mineral, said to have been so named from its resembling in its medicinal effects the root of the *Convolvulus turpethum*.

290. CHLORIDES OF MERCURY.—The chlorides are the most important of the compounds of mercury, one chloride being *calomel* (HgCl or Hg_2Cl_2) and the other *corrosive sublimate* ($HgCl_2$). Vapour of mercury burns in chlorine gas, corrosive sublimate being produced.*

Corrosive sublimate, *chloride of mercury*, *bichloride* or *perchloride of mercury*, or *mercuric chloride*, is manufactured by heating 2 parts by weight of mercury with 3 parts of strong sulphuric acid, and evaporating to dryness, to obtain mercuric sulphate—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2,$$

which is mixed with 1½ part of common salt and heated in glass vessels ($HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$), when sodium sulphate is left, and the corrosive sublimate is converted into vapour, condensing on the cooler part of the vessel in lustrous colourless masses, which are very heavy (sp. gr. 5.4), and have a crystalline fracture. It fuses very easily (at 509° F., 265° C.) to a perfectly colourless liquid, which boils at 563° F. (295° C.), emitting an extremely acrid vapour, which destroys the sense of smell for some time. The specific gravity of its vapour is 140 ($H = 1$); and that calculated from the formula $HgCl_2$ is 135.5. This vapour condenses in fine needles, or sometimes in octahedra. Corrosive sublimate dissolves in three times its weight of boiling water, but requires 16 parts of cold water, so that the hot solution readily deposits long four-sided prismatic crystals of the salt. It is remarkable that alcohol and ether dissolve corrosive sublimate much more easily than water, boiling alcohol dissolving about an equal weight of the chloride, and cold ether taking up one-third of its weight. By shaking the aqueous solution with ether, the greater part of the corrosive sublimate will be removed, and will remain dissolved in the ether which rises to the surface. Water, in which sal-ammoniac has been dissolved, will take up corrosive sublimate more easily than pure water, a soluble double chloride (*sal alembroth*) being formed, which may be obtained in tabular crystals of the composition $HgCl_2.6NH_4Cl.H_2O$. A solution of corrosive sublimate in water containing sal-ammoniac is a very efficacious *bug-poison*.

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* Two volumes of vapour of corrosive sublimate contain 2 volumes of mercury vapour (see note to page 407) and 2 volumes of chlorine.

Sulphuric acid does not decompose mercuric chloride, though it attacks mercurous chloride. Hydrochloric acid combines with it, forming crystalline compounds $HCl.HgCl_2$ and $HCl.2HgCl_2$, which lose HCl when exposed to air.

A crystalline compound, $HgCl_2.H_2SO_4$, is formed by the action of hydrochloric acid on mercuric sulphate.

The poisonous properties of corrosive sublimate are very marked, so little as three grains having been known to cause death in the case of a child. The white of egg is commonly administered as an antidote, because it is known to form an insoluble compound with corrosive sublimate, so as to render the poison inert in the stomach. The compound of albumen with corrosive sublimate is also much less liable to putrefaction than albumen itself, and hence corrosive sublimate is sometimes employed for preserving anatomical preparations and for preventing the decay of wood (by combining with the vegetable albumen of the sap).

Mercuric chloride unites with many other chlorides to form soluble double salts, and with mercuric oxide, forming several *oxychlorides*, which have no useful applications.

Mercuric chloride has been found native in one of the Molucca Islands.

White precipitate, employed for destroying vermin, is deposited when a solution of corrosive sublimate is poured into an excess of solution of ammonia; $HgCl_2 + 2NH_3 = NH_4Cl + NH_2Hg''Cl$ (*white precipitate*).

The true constitution of white precipitate has been the subject of much discussion, but the changes which it undergoes, under various circumstances, appear to lead to the conclusion that it represents ammonium chloride, NH_4Cl, in which half of the hydrogen has been displaced by mercury. When boiled with potash, it yields ammonia and mercuric oxide; $NH_2Hg''Cl + KHO = NH_3 + HgO + KCl$. If it be boiled with water, it is only partly decomposed in a similar manner, leaving a yellow powder having the composition $(NH_2HgCl).HgO$, produced according to the equation $2(NH_2HgCl) + H_2O = NH_4Cl + (NH_2HgCl).HgO$. A compound corresponding to this yellow precipitate, but containing mercuric chloride in place of oxide, is precipitated when ammonia is gradually added to solution of corrosive sublimate in large excess, the result being a compound of white precipitate with a molecule of undecomposed mercuric chloride, $(NH_2HgCl).HgCl_2$.

If white precipitate be heated to about 600° F. (315° C.), it evolves ammonia, and yields a sublimate of ammoniated mercuric chloride, $HgCl_2.NH_3$, leaving a red crystalline powder which is insoluble in water and in diluted acids, and is unchanged by boiling with potash; it may be represented as a compound of mercuric chloride with ammonia in which the whole of the hydrogen has been displaced by mercury, $N_2Hg''_3.2HgCl_2$. When strongly heated, white precipitate yields a sublimate of calomel; $6NH_2Hg''Cl = 3Hg_2Cl_2 + N_2 + 4NH_3$. White precipitate inflames in contact with chlorine or bromine. If it be mixed with about twice its weight of iodine and moistened with alcohol, an explosion occurs in about half an hour, from production of nitrogen iodide.

When solution of corrosive sublimate is added to a hot solution of sal-ammoniac, mixed with ammonia, a crystalline deposit is obtained on cooling the liquid, which is known as *fusible white precipitate*, and represents two molecules of ammonium chloride, in which one-fourth of the hydrogen has been displaced by mercury, its composition being $N_2H_6Hg''Cl_2$. The same compound is formed when white precipitate is boiled with solution of sal-ammoniac—

$$NH_2Hg''Cl + NH_4Cl = N_2H_6Hg''Cl_2.$$

The above compounds possess a special interest for the chemist, as they were among the first to attract attention to the mobility of the hydrogen in ammonia, which has since been so well exemplified in the artificial production of organic bases by the action of ammonia upon the iodides of the alcohol-radicals. The relation of these compounds to each other is here exhibited:—

White precipitate	$NH_2Hg''Cl$
Produced with corrosive sublimate in excess .	$(NH_2HgCl).HgCl_2$
,, by boiling with water	$(NH_2HgCl).HgO$
,, ,, sal-ammoniac . .	$N_2H_6Hg''Cl_2$
,, by heating to 600° F.	$N_2Hg''_3.2HgCl_2$

291. *Calomel, subchloride* or *protochloride of mercury*, or *mercurous chloride* (Hg_2Cl_2), unlike corrosive sublimate, is insoluble in water, so that it is precipitated when hydrochloric acid or a soluble chloride is added to mercurous nitrate. The simplest mode of manufacturing it consists in intimately mixing a molecular weight of corrosive sublimate with an atomic weight of metallic mercury, a little water being added to prevent dust, drying the mixture thoroughly, and subliming it; $HgCl_2 + Hg = Hg_2Cl_2$. But it is more commonly made by adding another atomic weight of mercury to the materials employed in the preparation of corrosive sublimate. Two parts by weight of mercury are dissolved, with the aid of heat, in 3 parts of oil of vitriol, and evaporated to dryness; $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$. The residue of mercuric sulphate is intimately mixed with 2 more parts of mercury, and the mixture afterwards triturated with 1½ part of common salt, until globules are no longer visible. The mixture is then heated, so that the calomel may pass off in vapour, which condenses as a translucent fibrous cake on the cool part of the subliming vessel, leaving sodium sulphate behind; $HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$. For medicinal purposes, the calomel is obtained in a very fine state of division by conducting the vapour into a large chamber so as to precipitate it in a fine powder by contact with a large volume of cold air. Steam is sometimes introduced to promote its fine division. Sublimed calomel always contains some corrosive sublimate, so that it must be thoroughly washed with water before being employed in medicine. When perfectly pure calomel is sublimed, a little is always decomposed during the process into metallic mercury and corrosive sublimate.

Calomel is met with either as a semi-transparent fibrous mass, or an amorphous powder, with a slightly yellow tinge. Light slowly decomposes it, turning it grey. It is heavier than corrosive sublimate (sp. gr. 7.18), and does not fuse before subliming; it may be obtained in four-sided prisms by slow sublimation. Diluted acids will not dissolve it, but boiling nitric acid gradually converts it into mercuric chloride and nitrate, which pass into solution. Boiling hydrochloric acid turns it grey, some mercury being separated, and mercuric chloride dissolved. Mercuric nitrate dissolves it, forming mercuric chloride and mercurous nitrate. Alkaline solutions convert it into black mercurous oxide, as is seen in *black-wash*, made by treating calomel with lime-water; $Hg_2Cl_2 + Ca(OH)_2 = Hg_2O + CaCl_2 + H_2O$. Solution of ammonia converts it into a grey compound (NH_2Hg_2Cl), which is the analogue of white precipitate ($NH_2Hg''Cl$), containing Hg_2 in place of Hg''. Calomel is found as *horn quicksilver* at Idria and Almaden, crystallised in rhombic prisms.

The vapour density of calomel has been found, by experiment, to be 117.5 ($H = 1$), whilst the formula Hg_2Cl_2 requires 235.5, which is explained by the dissociation of calomel vapour into 2 vols. $HgCl_2$ and 2 vols. Hg. The existence of metallic mercury in the vapour is shown by the deposition of minute globules of mercury on a very cold tube coated with gold and immersed in calomel vapour at 440° C.

Mercurous iodide, Hg_2I_2, is a green unstable substance, formed when iodine is triturated with an excess of mercury and a little alcohol, or by precipitating mercurous nitrate with potassium iodide. With care, it may be sublimed in yellow crystals, isomorphous with mercurous chloride, but if sharply heated, it is decomposed into Hg and HgI_2. Potassium iodide decomposes it in a similar way, dissolving the mercuric iodide.

Mercuric iodide, or *iodine scarlet*, HgI_2, is the bright red precipitate produced with mercuric chloride and potassium iodide. At the moment of precipitation it is yellow, rapidly becoming fawn-coloured and red. When the dry mercuric iodide is heated, it becomes bright yellow, and remains so on cooling until touched with a hard body, when it becomes red again, the colour spreading from the point touched. Under the microscope, the red iodide is seen to be octahedral and the yellow to consist of rhombic tables. When the yellow iodide is heated, it fuses easily, becomes brown, and is converted into a colourless vapour which condenses in yellow crystals on a cold surface.

A very beautiful experiment is made by gently heating mercuric iodide in a large porcelain crucible covered with a dial-glass; the yellow iodide is deposited in crystals projecting from the under surface of the glass, and if this be placed on the table with the crystals upwards, and some of these be touched with a needle, the red spots appear like poppies among corn, and the blush gradually spreads over the entire field, attended by a rustling movement caused by the change in crystalline form.*

The transformation of the yellow into the red iodide evolves heat. Mercuric iodide dissolves in hot alcohol, and crystallises in red octahedra. Ether also dissolves it. It is freely soluble in solutions of mercuric chloride and potassium iodide. The latter yields yellow prisms of $2(HgI_2.KI).3Aq$. The solution of this salt mixed with potash forms *Nessler's solution*, which gives a brown precipitate with very minute quantities of ammonia—

$$2HgI_2 + 3KHO + NH_3 = NHg_2I.H_2O + 3KI + 2H_2O.$$

The vapour density of mercuric iodide is of course very high, being 15.68 times that of air, showing that the formula HgI_2 represents two volumes.

292. SULPHIDES OF MERCURY.—When mercury is triturated with sulphur, the black *subsulphide of mercury*, or *mercurous sulphide* (Hg_2S), is formed; it was termed by old writers *Ethiop's mineral*, and is an unstable compound easily resolvable into metallic mercury and *mercuric sulphide* (HgS). The latter has been mentioned as the principal ore of mercury, and is important as composing *vermilion*. The native mercuric sulphide, or *cinnabar*, is found sometimes in amorphous masses, sometimes crystallised in six-sided prisms varying in colour from dark brown to bright red. It may be distinguished from most other minerals by its great weight (sp. gr. 8.2), and by its red colour when scraped with a knife. Neither hydrochloric nor nitric acid, separately, will dissolve it, but a mixture of the two dissolves it as mercuric chloride, with separation of sulphur. Some specimens of cinnabar have a bright red colour, so that they only require grinding and levigating to be used as vermilion; and if the brown cinnabar in powder be heated for some time to 120° F. (49° C.) with a solution of sulphur in potash, it is converted into vermilion.

Of the artificial mercuric sulphide there are two varieties—the black, which is precipitated when corrosive sublimate is added to hydrosulphuric acid or a soluble sulphide, and the red (vermilion), into which the black variety is converted by sublimation, or by prolonged contact with solutions of alkaline sulphides containing excess of sulphur, though, so far as is known, the conversion is effected without chemical change, the red sulphide having the same composition as the black. In Idria and Holland, 6 parts of mercury and 1 of sulphur are well agitated together in revolving casks for several hours and the black sulphide thus obtained is sublimed in tall earthen pots closed with iron plates, when the vermilion is deposited in the upper part of the pots, and is afterwards ground and levigated. The sublimed vermilion, however, is generally inferior to that obtained by the wet process, of which there are several modifications. One of the processes consists in triturating 300 parts of mercury with 114 parts of sulphur for two or three hours, and digesting the black product, at about 120° F., with 75 parts of caustic potash and 400 of water until it has acquired a fine red colour. The permanence of vermilion paint is, of course, attributable to the circumstance that it resists the action of light, of oxygen, carbonic acid, aqueous vapour, and even of the sulphuretted hydrogen, and sulphurous or sulphuric acid which contaminate the air of towns, whereas the red paints containing lead are blackened by sulphuretted hydrogen, and all vegetable and animal reds are liable to be bleached by atmospheric oxygen and by sulphurous acid.

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* The author is indebted for this experiment to Mr. Herbert Jackson, of King's College.

The conversion of the black mercuric sulphide into the red form is quickly effected by boiling it with freshly prepared ammonium polysulphide (made by saturating ammonia with H_2S and dissolving sulphur in the liquid, gently warmed, until it has a dark sherry colour). If this solution be poured upon the freshly precipitated black sulphide, and boiled for a minute, the sulphide assumes a crystalline appearance and a bright vermilion colour (Herbert Jackson).

If the black sulphide be boiled with potassium sulphide and potash, it is dissolved, and the solution deposits white needles of $HgS.K_2S.5H_2O$, which are decomposed by water.

When the black precipitated mercuric sulphide is boiled with solution of corrosive sublimate, it is converted into a white *chlorosulphide of mercury*, $HgCl_2.2HgS$, which is also formed when a small quantity of hydrosulphuric acid is added to corrosive sublimate, becoming yellow, brown, and black on adding more H_2S.

Vermilion may be prepared by adding $HgCl_2$ to a slight excess of dilute ammonia, nearly dissolving the precipitate in sodium thiosulphate (hyposulphite) and heating, when a bright yellow precipitate is obtained, which becomes bright red on boiling.

It is remarkable that the density of its vapour indicates that the molecule of vermilion, HgS, occupies 3 volumes instead of 2, containing 2 volumes of mercury vapour combined with 1 volume of sulphur vapour. The anomaly might be explained on the supposition that the high temperature requisite to convert the vermilion into vapour suffices to suspend the attraction between its elements, so that the vapour of which the specific gravity is taken is not really that of the compound of mercury and sulphur (which should occupy 2 volumes), but a *mixture* of the 2 volumes of mercury vapour and 1 volume of sulphur vapour, occupying 3 volumes. This view of the temporary decomposition of the vapour receives some slight support from the convertibility of the black into the red sulphide by sublimation.

PLATINUM.

Pt = 197.1 parts by weight.

293. Platinum (*platina*, Spanish diminutive of silver) is remarkable for (1) its high specific gravity of 21.5; (2) its very high fusing point, about 2000° C.; (3) its slight expansion when heated, which allows it

to be sealed into glass without cracking by unequal contraction on cooling; (4) its being unchanged by air at all temperatures; (5) its resistance to the action of strong acids; (6) its power of inducing the combination of oxygen with other bodies; (7) its being found in nature only in the metallic state. It is found distributed in flattened grains through alluvial deposits similar to those in which gold is found; indeed, these grains are generally accompanied by grains of gold, and of a group of very rare metals only found in platinum ores, viz., palladium, iridium, osmium, rhodium, and ruthenium. Russia furnishes the largest supply of platinum from the Ural Mountains, but smaller quantities are obtained from Brazil, Peru, Borneo, Australia, and California.

The process for obtaining the platinum in a marketable form is rather a chemical than a metallurgic operation. The ore, containing the grains of platinum and the associated metals, is heated with a dilute mixture of hydrochloric and nitric acids, by which the platinum is converted into platinic chloride ($PtCl_4$) and dissolved, whilst the iridium and osmium are left in the residue. The solution is evaporated to dryness, and the residue heated to 125° C., when the palladic chloride, $PdCl_4$, becomes palladous chloride, $PdCl_2$, which is not precipitated by ammonium chloride. The chlorides are dissolved in water, and the solution is mixed with some ammonium chloride, which combines with the platinic chloride to form a yellow insoluble salt (ammonio-platinic chloride, $2NH_4Cl.PtCl_4$).* This precipitate is collected, washed, and heated to redness, when all its constituents, except the platinum, are expelled in the form of gas, that metal being left in the peculiar porous condition in which it is known as *spongy platinum*. To convert this into compact platinum is by no means an easy task, on account of the infusibility of the metal, for it remains solid at the very highest temperatures of our furnaces. The spongy platinum is finely powdered in a wooden mortar (as it would cohere into metallic spangles in one of a harder material) and rubbed to a paste with water; this paste is then rubbed through a sieve to render it perfectly smooth and uniform, and introduced into a cylinder of brass, in which it is subjected to pressure so as to squeeze out the water, and cause the minute particles of platinum to cohere into a somewhat compact disc; this disc is then heated to whiteness, and beaten into a compact metallic ingot by a heavy hammer; it is then ready for forging.

This method is now modified by fusing the ore with 6 parts of lead, and treating the alloy with dilute nitric acid (1 : 8), which dissolves most of the lead, together with copper, iron, palladium, and rhodium. The residue, containing platinum, lead, and iridium, is treated with dilute aqua regia, which leaves the iridium undissolved. The lead is precipitated by sulphuric acid, and the solution of platinic chloride treated as above.

Another process for obtaining platinum from its ores is based upon the tendency of this metal to dissolve in melted lead. The platinum ore is fused in a small reverberatory furnace, with an equal weight of sulphide of lead and the same quantity of oxide of lead, when the sulphur and oxygen escape as sulphurous acid gas, and the reduced lead dissolves the platinum, leaving undissolved a very heavy alloy of osmium and iridium, which sinks to the bottom. The upper part of the alloy of lead and platinum is then ladled out and cupelled (page 390), when the latter metal is left in a spongy condition, the lead being removed in the form of oxide. The platinum is then fused by the aid of the oxyhydrogen blowpipe, in a furnace made of lime (fig. 263), whence it is poured into an ingot mould made of gas carbon. The melted platinum absorbs oxygen mechanically like melted silver, and evolves it again on cooling (see page 391). Platinum articles are now frequently made from the fused metal, instead of from that which has been welded.

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* When rhodium is present, the liquid from which this precipitate has been deposited will have a rose colour. The precipitate is then mixed with bisulphate of potassium and a little bisulphate of ammonium, and heated to redness in a platinum dish. The rhodium is then converted into a double sulphate of rhodium and potassium, which may be removed from the spongy platinum by boiling with water.

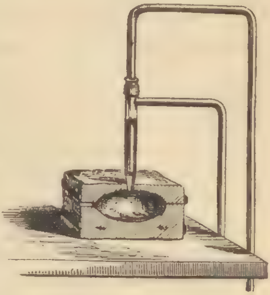
Fig. 263.

Its resistance to the action of high temperatures and of most chemical agents renders platinum of the greatest service in chemical operations. It will be remembered that platinum stills are employed, even on the large scale, for the concentration of sulphuric acid. In the form of basins, small crucibles, foil, and wire, this metal is indispensable to the analytical chemist. Unfortunately, it is softer than silver, and therefore ill adapted for wear, and is so heavy that even small vessels must be made very thin in order not to be too heavy for a delicate balance. Commercial platinum generally contains a little iridium, which hardens it and increases its elasticity. Its malleability and ductility are very considerable, so that it is easily rolled into thin foil and drawn into fine wires; in ductility it is surpassed only by gold and silver, and it has been drawn, by an ingenious contrivance of Wollaston's, into wire of only $\frac{1}{30000}$th of an inch in diameter, a mile of which (notwithstanding the high specific gravity of the metal) would only weigh a single grain. This remarkable extension of the metal was effected by casting a cylinder of silver around a very thin platinum wire obtained by the ordinary process of wire-drawing; when the cylinder of silver, with the platinum wire in its centre, was itself drawn out into an extremely thin wire, of course the platinum core would have become inconceivably thin, and when the silver casing was dissolved off by nitric acid, this minute filament of platinum was left. Platinum is sometimes employed for the touch-holes of fowling-pieces on account of its resistance to corrosion. An alloy of 4 parts platinum, 3 parts silver, and 1 part copper is used for pens.

The remarkable power possessed by platinum, of inducing chemical combination between oxygen and other gases, has already been noticed. Even the compact metal possesses this property, as may be seen by heating a piece of platinum foil to redness in the flame of a gauze gas-burner, rapidly extinguishing the gas, and turning it on again, when the cold stream of gas will still maintain the metal at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum.

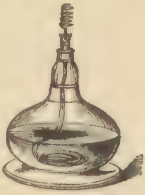
Fig. 264.

A similar experiment may be made by suspending a coil of platinum wire in the flame of a spirit lamp (fig. 264), and suddenly extinguishing the flame, when the metal is intensely heated, by placing the mouth of a test-tube over it; the wire will continue to glow by inducing the combination of the spirit vapour with oxygen on its surface. By substituting a little ball of spongy platinum for the coil of platinum wire, and mixing some fragrant essential oil with the spirit, an elegant perfuming lamp has been contrived. Upon the same principle an instantaneous light apparatus has been made, in which a jet of hydrogen gas is kindled by falling upon a fragment of cold spongy platinum, which at once ignites it by inducing its combination with the oxygen condensed within the pores of the metal. Spongy platinum is obtained in a very active form by heating the ammonio-chloride of platinum very gently in a stream of coal gas or hydrogen as long as any fumes of hydrochloric acid are evolved.

If platinum be precipitated in the metallic state from a solution, it is obtained in the form of a powder, called platinum black, which possesses this power of promoting combination with oxygen in the highest perfection. This form of platinum may be obtained by boiling solution of platinic chloride with Rochelle salt (potassium sodium tartrate), or by dropping it into a boiling mixture of 3 vols. glycerin and 2 vols. KHO of sp. gr. 1.08, when the platinum black is precipitated, and must be filtered off, washed, and dried at a gentle heat.

Platinum in this form is capable of absorbing 800 times its volume of oxygen, which does not enter into combination with it, but is simply condensed into its pores, and is available for combination with other bodies. A jet of hydrogen allowed to pass on to a grain or two of this powder is kindled at once, and if a few particles of it be thrown into a mixture of hydrogen and oxygen, explosion immediately follows. A drop of alcohol is also inflamed when allowed to fall upon a little of the powder. Platinum black loses its activity after having been heated to redness. Recent experiments by Berthelot indicate that platinum black is really an oxide; he concludes that the combustion of hydrogen and oxygen in presence of platinum is explained by the formation, at first, of an unstable hydride of platinum, with development of heat, which is oxidised with a still further development of heat. By a continued repetition of these changes, the platinum is raised to the temperature necessary for ignition.

Although platinum resists the action of hydrochloric and nitric acids, unless they are mixed, and is unaffected at the ordinary temperature by other chemical agents, it is easily attacked at high temperatures by phosphorus, arsenic, carbon, boron, silicon, and by a large number of the metals; the caustic alkalies and alkaline earths also corrode it when heated, so that some discretion is necessary in the use of vessels made of this costly metal. When platinum is alloyed with 10 parts of silver, both metals may be dissolved by nitric acid.

If platinum be dissolved in 4 or 5 parts of melted tin, and the alloy boiled with hydrochloric acid mixed with an equal bulk of water, glistening scales are left, resembling graphite, and soiling the fingers. This contains platinum, tin, chlorine, hydrogen, and oxygen. By treatment with warm dilute ammonia, it becomes brownish, and when dried in a vacuum over sulphuric acid, has the composition $Pt_2Sn_3O_4H_2$. When this is heated in dry oxygen, it becomes $Pt_2Sn_3O_4$. Heated in hydrogen it leaves a greyish almost infusible powder containing Pt_2Sn_3.

294. OXIDES OF PLATINUM.—Only one compound of platinum with oxygen is known in the separate state, the other having been obtained in combination with water. *Platinous oxide*, PtO, is precipitated as a black hydrate by decomposing platinous chloride with potash, and neutralising the solution with dilute sulphuric acid. It is a feeble base, and decomposes when heated, leaving metallic platinum. *Platinic oxide*, PtO_2, is also a weak base.

Platinic hydrate, $Pt(HO)_4$, is obtained by boiling platinic chloride with potash, and treating the precipitate with acetic acid; this leaves a nearly white powder, $Pt(HO)_4.2H_2O$. At 100° C. this becomes brown $Pt(HO)_4$. Acids dissolve it, forming platinic salts. Alkalies dissolve it, forming platinates. Heat reduces the oxides and hydrates to metallic platinum.

Sodium platinate, $Na_2Pt_3O_7.6Aq$, may be crystallised from a solution of the acid in soda. *Calcium platinate* is convenient for the separation of platinum from iridium, which is generally contained in the commercial metal; for this purpose, the platinum is dissolved in nitro-hydrochloric acid, the solution evaporated till it solidifies on cooling, the mixed chlorides of iridium and platinum dissolved in water, and decomposed with an excess of lime *without exposure to light;* the platinum then passes into solution as calcium platinate, and the platinic acid may be separated as a calcium salt from the filtered solution, by exposure to light. If platinic oxide be dissolved in diluted sulphuric acid and the solution mixed with excess of ammonia, a black precipitate of *fulminating platinum* is obtained, which detonates violently at about 400° F. This compound is said to have a composition corresponding to the formula $N_2H_2Pt^{iv}.4H_2O$, or a combination of water with a double molecule of ammonia (N_2H_6), in which 4 atoms of hydrogen are replaced by 1 atom of tetrad platinum.

295. CHLORIDES OF PLATINUM.—The *perchloride*, or *platinic chloride* ($PtCl_4$), is the most useful salt of the metal, and may be prepared by dissolving scraps of platinum-foil in a mixture of four measures of hydrochloric acid with one of nitric acid (100 grs. or 6.5 grms. of platinum require 2 measured ounces or 56 c.c. of hydrochloric acid), evaporating the liquid at a gentle heat to the consistence of a syrup, redissolving in hydrochloric acid, and again evaporating to expel excess of nitric acid. The syrupy liquid solidifies, on cooling, to a red-brown mass, which is very deliquescent, and dissolves easily in water or alcohol to a red-brown solution. If the concentrated solution be allowed to cool before all the free hydrochloric acid has been expelled, long brown prismatic crystals of a combination of platinic chloride with hydrochloric acid are obtained ($PtCl_4.2HCl.6Aq$). Platinic chloride is remarkable for its disposition to form sparingly soluble double chlorides with the chlorides of the alkali metals and the hydrochlorates of organic bases, a property of great value to the chemist in effecting the detection and separation of these bodies.

A good example of this has lately been afforded in the separation of potassium, rubidium, and cæsium. The chlorides of these three metals having been separated from the various other salts contained in the mineral water in which they occur, are precipitated with platinic chloride, which forms combinations with all the three chlorides. The platino-chloride of potassium is more easily dissolved by boiling water than those of rubidium and cæsium, and is removed by boiling the mixed precipitate with small portions of water as long as the latter acquires a yellow colour. The remaining platino-chlorides of rubidium and cæsium are then heated in a current of hydrogen, which reduces the platinum to the metallic state, and the chlorides may then be extracted by water, in which they are very soluble.

Potassium platinic chloride ($2KCl.PtCl_4$) forms minute yellow octahedral crystals; those of rubidium and cæsium have a similar composition and crystalline form. *Sodium platinic chloride* differs from these in being very soluble in water and alcohol; it may be crystallised in long red prisms, having the composition $2NaCl.PtCl_4.6Aq$. *Ammonium platinic chloride* ($2NH_4Cl.PtCl_4$) has been already noticed as the form in which platinum is precipitated in order to separate it from other metals. It crystallises, like the potassium-salt, in yellow octahedra, which are very sparingly soluble in water and insoluble in alcohol. It is the form into which nitrogen is finally converted in analysis in order to determine its weight. When heated to redness, this salt leaves a residue of spongy platinum.

Platinic chloride is sometimes used for browning gun-barrels, &c., under the name of *muriate of platina*. Silver nitrate, added in excess to platinic chloride containing HCl, precipitates all the platinum as $2AgCl.PtCl_4$, a yellow precipitate decomposed by water.

Protochloride of platinum, or *platinous chloride* ($PtCl_2$).—Platinic chloride may be heated to 450° F. (232° C.) without decomposition, but above that temperature it evolves chlorine, and is slowly converted into the platinous chloride, which is reduced, at a much higher temperature, to the metallic state. Platinous chloride forms a dingy green powder, which is insoluble in water and in nitric and sulphuric acids, but dissolves in hot hydrochloric acid, and in solution of platinic chloride, yielding in the former a bright red, in the latter a very dark brown-red solution. Platinous chloride is capable of absorbing ethylene, C_2H_4. At 250° C. it absorbs CO and forms crystalline compounds. Its solution in hydrochloric acid is not precipitated by potassium chloride, but a soluble double chloride ($2KCl.PtCl_2$) may be crystallised from the liquid. If ammonium chloride be added to the hydrochloric solution, a double salt, $2NH_4Cl.PtCl_2$, may be obtained in yellow crystals by evaporation. If, instead of ammonium chloride, free ammonia be added in excess to the boiling solution of platinous chloride in hydrochloric acid, brilliant green needles (*green salt of Magnus*) are deposited on cooling, which contain the elements of platinous chloride and ammonia, $PtCl_2(NH_3)_2$; but from the behaviour of this compound with chemical agents, its true formula would appear to be $N_2H_6Pt''Cl_2$, in which the place of 2 atoms of hydrogen in 2 molecules of sal-ammoniac is occupied by platinum. By heating this salt with an excess of ammonia, the solution, on cooling, deposits yellowish-white prismatic crystals of *hydrochlorate of diplatosamine*, $N_4H_{10}Pt''.2HCl.Aq$, the production of which may be represented by the equation $N_2H_6Pt''Cl_2 + 2NH_3 = N_4H_{10}Pt''.2HCl$. By decomposing a solution of this salt with silver sulphate, the *sulphate of diplatosamine* is obtained—

$$N_4H_{10}Pt''.2HCl + Ag_2SO_4 = N_4H_{10}Pt''.H_2SO_4 + 2AgCl.$$

When the solution of diplatosamine sulphate is treated with barium hydrate, barium sulphate is precipitated, and a powerfully alkaline solution is obtained, which yields crystals of *diplatosamine hydrate*, $N_4H_{10}Pt''.2H_2O$, a strong alkali which may be regarded as a compound of water with 4 molecules of ammonia (N_4H_{12}), in which two atoms of hydrogen are replaced by platinum. The diplatosamine hydrate has a strong resemblance to the alkalies, eagerly absorbing carbonic acid from the air, and expelling ammonia from its salts. When the hydrate of diplatosamine is heated to 110° C. it gives off water and ammonia, and becomes converted into a grey insoluble substance, which is *platosamine hydrate*, $N_2H_4Pt''.H_2O$, and may be regarded as a compound of water with a double molecule of ammonia (N_2H_6), in which one-third of the hydrogen is replaced by platinum. This substance is also a base, and forms salts, most of which are insoluble; the *sulphate of platosamine*, $N_2H_4Pt.H_2SO_4.Aq$, may be regarded as ammonium sulphate, $(NH_4)_2SO_4$, in which 2 atoms of the hydrogen are replaced by platinum. The *hydrochlorate of platosamine* ($N_2H_4Pt.2HCl$) is isomeric with the green salt of Magnus, and may be obtained from that compound by dissolving in a hot solution of ammonium sulphate from which it crystallises on cooling.*

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* The salts of diplatosamine are distinguished from those of platosamine by the action of nitrous acid, which gives a fine blue or green precipitate or coloration with the former. For the cause of this change, and for many other interesting points in the history of these

If the *platosamine hydrochlorate*, suspended in boiling water, be treated with chlorine, it is converted into *platinamine hydrochlorate*, $N_2H_2Pt^{iv}.4HCl$. The conversion of the platosamine hydrochlorate into platinamine hydrochlorate may be represented by the equation $N_2H_4Pt.2HCl + Cl_2 = N_2H_2Pt.4HCl$. By boiling the hydrochlorate of platinamine with silver nitrate, it is converted into *platinamine nitrate*, $N_2H_2Pt(HNO_3)_4$; and when this is dissolved in boiling water and decomposed by ammonia, the *platinamine hydrate* ($N_2H_2Pt.4H_2O$) is obtained in yellow prismatic crystals, having the same composition as that assigned to fulminating platinum.

Several other platinum compounds derived from ammonia have been obtained, but cannot at present be so conveniently classified. The following table exhibits the composition of those here enumerated, the platinum as it exists in platinous chloride ($PtCl_2$), occupying the place of 2 atoms of hydrogen, being represented by Pt'', and the platinum as it exists in platinic chloride ($PtCl_4$), occupying the place of 4 atoms of hydrogen, by Pt^{iv}:—

Platosamine hydrate	$N_2H_4Pt''.H_2O$
,, hydrochlorate . . .	$N_2H_4Pt''.2HCl$
,, sulphate	$N_2H_4Pt''.H_2SO_4Aq$
Platinamine hydrate	$N_2H_2Pt^{iv}.4H_2O$
,, hydrochlorate . . .	$N_2H_2Pt^{iv}.4HCl$
Diplatosamine hydrate	$N_4H_{10}Pt''.2H_2O$
,, hydrochlorate . .	$N_4H_{10}Pt''.2HCl.Aq$
,, sulphate	$N_4H_{10}Pt''.H_2SO_4$

Some of the salts of *diplatinamine* ($N_4H_8Pt^{iv}$) have been obtained, this base being derived from 4 molecules of ammonia in which H_4 have been replaced by Pt^{iv}.

Platinic iodide, PtI_4, is a dark brown amorphous substance which is soluble in HI, yielding a purple-red solution containing $2HI.PtI_4.9Aq$, which may be crystallised. Hence the dark red colour when an acid solution of $PtCl_4$ is added to potassium iodide.

The *sulphides of platinum* correspond in composition to the oxides and chlorides, and may be obtained by the action of hydrosulphuric acid upon the respective chlorides, as black precipitates. PtS_2 combines with alkaline sulphides to form soluble compounds. $K_2S.3PtS.PtS_2$ is obtained by fusing spongy platinum with KHO and sulphur.

Platinum phosphide, PtP_2, and *arsenide*, $PtAs_2$, are lustrous metallic bodies formed by direct combination at a high temperature.

296. PALLADIUM ($Pd = 105.7$) is found in small quantity associated with native gold and platinum. It presents a great general resemblance to platinum, but is distinguished from it by being far more easily oxidised, and by its forming an insoluble cyanide. This circumstance is taken advantage of in separating palladium from the platinum ores, for which purpose the solution from which the greater part of the platinum has been precipitated by ammonium chloride (page 416) is neutralised with sodium carbonate, and mixed with solution of mercuric cyanide, $Hg(CN)_2$, when a yellowish precipitate of palladium cyanide is obtained, yielding spongy palladium when heated, which may be welded into a compact form in the same manner as platinum. When alloyed with native gold, palladium is separated by fusing the alloy with silver, and boiling it with nitric acid, which leaves the gold undissolved. The silver is precipitated from the solution as chloride, by adding sodium chloride, and metallic zinc is placed in the liquid, which precipitates the palladium, lead, and copper as a black powder. This is dissolved in nitric acid, and the solution mixed with an excess of ammonia, which precipitates the lead oxide, leaving the copper and palladium in solution. On adding hydrochloric acid in slight excess, a yellow precipitate of *palladamine hydrochlorate* ($N_2H_4Pd.2HCl$) is obtained, which leaves metallic palladium when heated.

Palladium is harder than platinum and much lighter (sp. gr. 11.5); it is malleable and ductile like that metal, and somewhat more fusible, though it cannot be melted in an ordinary furnace. It is unchangeable in air unless heated, when it becomes blue from superficial oxidation, but regains its whiteness when further heated, the oxide being decomposed. Unlike platinum, it may be dissolved by nitric acid, forming *palladium nitrate*, $Pd(NO_3)_2$, which is sometimes employed in analysis

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platinum compounds, the reader is referred to the elaborate and accurate memoir by Hadow, *Journal of the Chemical Society*, August 1866.

for precipitating iodine from the iodides, in the form of black *palladium iodide* (PdI_2). Palladium is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with twice its weight of silver, it is used for small weights.

Palladium, at a slightly elevated temperature, absorbs, mechanically, many times its volume of hydrogen. Hammered palladium foil condenses 640 times its volume of hydrogen, below 212° F., though it has not the power of absorbing oxygen or nitrogen. Foil made from fused palladium only absorbs 68 times its volume of hydrogen. The sp. gr. of the hydrogen as it exists in the palladium is 0.62. The highest number obtained for the atomic heat of the hydrogen in palladium was 5.88. The absorption of 1 grm. of hydrogen by palladium evolves 9000 heat units. It is believed that the hydrogen combines with the palladium to form Pd_2H. The hydrogen in this condition is a very active reducing agent; it converts potassium chlorate into chloride, and potassium nitrate into nitrite.

Of the *oxides of palladium*, two correspond with those of platinum, and a basic *oxide* (PdO) has been obtained by gently heating the dioxide. *Palladic chloride* ($PdCl_4$) is very unstable, being easily decomposed, even in solution, into *palladous chloride* ($PdCl_2$) and free chlorine. Both the chlorides form double salts with the alkaline chlorides, those containing the *palladous chloride* ($PdCl_2$) having a dark green colour. Pulverulent *palladium carbide* is formed when the metal is heated in the flame of a spirit-lamp.

297. Rhodium ($Ro = 104.3$), another of the metals associated with the ores of platinum, has acquired its name from the red colour of many of its salts (ῥόδον, *a rose*). It is obtained from the solution of the ore in *aqua regia* by precipitating the platinum with ammonium chloride, neutralising with sodium carbonate, adding mercuric cyanide to separate the palladium, and evaporating the filtered solution to dryness with excess of hydrochloric acid. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed, the rhodium is reduced to the metallic state, and the sodium chloride may be washed out with water, leaving a grey powder of metallic rhodium, which is fused by the oxyhydrogen blowpipe with greater difficulty than platinum, and forms a very hard malleable metal not dissolved even by *aqua regia*, although this acid dissolves it in ores of platinum, because it is alloyed with other metals. If platinum be alloyed with 30 per cent. of rhodium, however, it is not affected by *aqua regia*, which will probably render the alloy useful for chemical vessels. Rhodium may be brought into solution by fusing it with bisulphate of potash, when sulphurous acid gas escapes, and a double sulphate of rhodium and potassium is formed, which gives a pink solution with water. Finely divided rhodium is oxidised when heated in air. It appears to form two oxides, the *monoxide* (RoO), which is very little known, and the *sesquioxide* (Ro_2O_3), obtained by fusing rhodium with potassium carbonate and nitre, and washing the fused mass with water, which leaves an insoluble compound of the sesquioxide with potash; on treating this with hydrochloric acid, the sesquioxide of rhodium is left. It is not decomposed by heat, and is insoluble in acids, though it is a basic oxide, and its salts, which have a red colour, are obtained by indirect methods.

Rhodium trichloride ($RoCl_3$) has a brownish-black colour, and does not crystallise. Its aqueous solution is red, and it forms crystallisable double salts with the alkaline chlorides, which have a fine red colour. The double chloride of rhodium and sodium ($3NaCl.RoCl_3$) is prepared by heating a mixture of pulverulent rhodium and sodium chloride in a current of chlorine. It crystallises in red octahedra with 9Aq. On boiling a solution of rhodium trichloride with ammonia in excess, a yellow ammoniated salt ($RoCl_3.5NH_3$) may be crystallised out, from which metallic rhodium may be obtained by ignition.

With sulphur, rhodium combines energetically at a high temperature; a monosulphide and a sesquisulphide have been obtained.

An alloy of gold with between 30 and 40 per cent. of rhodium has been found in Mexico.

298. Osmium ($Os = 200$) is characterised by its yielding a very volatile acid oxide (osmic anhydride, OsO_4), the vapours of which have a very irritating odour (ὀσμή, *odour*). It occurs in the ores of platinum in flat scales, consisting of an alloy of osmium, iridium, ruthenium, and rhodium. This alloy is also found associated with native gold, and, being very heavy, it accumulates at the bottom of the crucible in which the gold is melted. The osmium alloy is extremely hard, and

has been used to tip the points of gold pens. When a grain of it happens to be present in the gold which is being coined, it often seriously injures the die. When the platinum ore is treated with *aqua regia*, this alloy is left undissolved, together with grains of chrome-iron ore and titanic iron. To extract the osmium from this residue, it is heated in a porcelain tube through which a current of dry air is passed, when the osmium is converted into osmic anhydride, the vapour of which is carried forward by the current of air and condensed in bottles provided to receive it. The *osmic anhydride* forms colourless prismatic crystals which fuse and volatilise below the boiling point of water, yielding a most irritating vapour resembling chlorine. It is very soluble in water, giving a solution which exhales the same odour and stains the skin black; tincture of galls gives a blue precipitate with the solution. Its acid properties are feeble, for it neither reddens litmus nor decomposes the carbonates, and its salts are decomposed by boiling their solutions. By adding hydrosulphuric acid to a solution of osmic acid, the *osmium tetrasulphide* (OsS_4) is obtained as a black precipitate, and if this be carefully dried and heated in a crucible made of gas-carbon, *metallic osmium* is obtained as a brittle mass (sp. gr. 21.4), which is not fused even by the oxyhydrogen blowpipe, and is not soluble in acids. When obtained by other processes in a finely divided state, osmium oxidises even at the ordinary temperature, and emits the odour of osmic anhydride. In this state, also, it may be dissolved by nitric acid, which converts it into osmic acid.

By passing a mixture of CO and vapour of OsO_4 through a red-hot porcelain tube, amorphous osmium is obtained, and may be converted into the crystalline form by fusing it with tin and dissolving in HCl, when blue lustrous cubical crystals of osmium are obtained, which scratch glass and are heavier than any other body, having the specific gravity 22.48.

By dissolving osmic anhydride in potash and adding alcohol, the latter is oxidised at the expense of the potassium osmiate, and rose-coloured octahedral crystals of *potassium osmite* ($K_2OsO_4.2Aq$) are obtained; the osmious acid has not been isolated. A monoxide and a dioxide of osmium have been obtained.

Osmium appears to form four chlorides—*dichloride* ($OsCl_2$), *trichloride* ($OsCl_3$), *tetrachloride* ($OsCl_4$), and *hexachloride* ($OsCl_6$). The dichloride and tetrachloride are formed by the direct combination of chlorine with osmium; the former sublimes in green needles, which yield a blue solution in water, soon absorbing oxygen from the air and becoming converted into tetrachloride. By heating a mixture of pulverulent osmium with potassium chloride in a current of chlorine, a double chloride of osmium and potassium ($2KCl.OsCl_4$) is obtained, which is sparingly soluble, and crystallises in octahedra like the corresponding salt of platinum. When decomposed with silver nitrate, it gives a dark green precipitate ($2AgCl.OsCl_4$).

299. RUTHENIUM ($Ru = 104.2$).*—In the process of extracting osmium from the residue left on treating the platinum ore with *aqua regia*, by heating in a current of air, square prismatic crystals of *ruthenium dioxide* (RuO_2) are deposited nearer to the heated portion of the tube than the osmic anhydride, for the dioxide is not itself volatile, being only carried forward mechanically. When ruthenium dioxide is heated in hydrogen, *metallic ruthenium* is obtained as a hard, brittle, almost infusible metal, which is scarcely affected even by *aqua regia*. The *monoxide of ruthenium* (RuO) is a dark grey powder insoluble in acids. The *sesquioxide* (Ru_2O_3) and the *dioxide* (RuO_2) have feebly basic properties. The sesquioxide is not decomposed by heat. The anhydrous dioxide is a greenish-blue powder. *Ruthenic anhydride* (RuO_3) is known only in combination with bases.

300. IRIDIUM ($Ir = 192.5$), named from Iris, *the rainbow*, in allusion to the varied colours of its compounds, has been mentioned above as occurring in the insoluble alloy from the platinum ores. It is also sometimes found separately, and occasionally alloyed with platinum, the alloy crystallising in octahedra, which are even heavier than platinum (sp. gr. 22.3). If the insoluble osmiridium alloy left by *aqua regia* be mixed with common salt and heated in a current of chlorine, a mixture of the sodio-chlorides of the metals is obtained, and may be extracted by boiling water. If the solution be evaporated and distilled with nitric acid, the osmium is distilled off as osmic acid, and by adding ammonium chloride to the residual solution, the iridium is precipitated as a dark red-brown ammonio-chloride, $2NH_4Cl.IrCl_4$, which leaves metallic iridium when heated. Like platinum,

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* A mineral found in Borneo, and named *laurite*, contains sulphides of ruthenium and osmium. It forms small lustrous granules.

it then forms a grey spongy mass, but is oxidised when heated in air, and may be fused with the oxyhydrogen blowpipe to a hard brittle mass (sp. gr. 22.4), which does not oxidise in air. Like rhodium, it is not attacked by *aqua regia*, unless alloyed with platinum. The product of the oxidation of finely divided iridium is air in the *sesquioxide* (Ir_2O_3), which is a black powder used for imparting an intense black to porcelain; it is insoluble in acids. The *monoxide* (IrO) is also more easily acted upon by alkalies than by acids; its solution in potash becomes blue when exposed to air, from the formation of the *dioxide* (IrO_2). The *trioxide* (IrO_3) is green. The *dichloride* ($IrCl_2$) and *tetrachloride* ($IrCl_4$) of iridium resemble the corresponding chlorides of platinum in forming double salts with the alkaline chlorides. There is also a *trichloride* ($IrCl_3$), the solution of which has a green colour, and gives a yellow precipitate with mercurous nitrate, and a blue precipitate, soon becoming white, with silver nitrate. Iridium resembles palladium in its disposition to combine with carbon when heated in the flame of a spirit-lamp.

An *iridio-platinum alloy* containing from 15 to 20 per cent. of iridium has been found very useful for making standard rules and weights, on account of its indestructibility, extreme rigidity, hardness, and high density.

The following table exhibits a general view of the analytical process by which the remarkable metals associated in the ores of platinum may be separated from each other, omitting the minor details which are requisite to ensure the purity of each metal:—

Analysis of the Ore of Platinum.

Boil with *aqua regia.*

<table>
<tr><td colspan="3">Dissolved.
PLATINUM, PALLADIUM, RHODIUM.
Add <i>ammonium chloride.</i></td><td colspan="4">Undissolved.
IRIDIUM, OSMIUM, RUTHENIUM.
Chrome iron, Titanic iron, &c.
Heat in a current of dry air.</td></tr>
<tr><td rowspan="2">Precipitated;
PLATINUM
as
$2NH_4Cl.PtCl_4$.</td><td colspan="2">Solution;
Neutralise with sodium carbonate; add <i>mercuric cyanide.</i></td><td rowspan="2">Volatilised;
OSMIUM
as OsO_4.</td><td rowspan="2">Carried forward by the current;
RUTHENIUM
as RuO_2.</td><td colspan="2">Residue;
Mix with <i>sodium chloride</i>, and heat in a current of <i>chlorine.</i>
Treat with <i>boiling water.</i></td></tr>
<tr><td>Precipitated;
PALLADIUM
as $PdCy_2$.</td><td>Solution;
Evaporate with <i>hydrochloric acid.</i>
Treat with <i>alcohol.</i>
Insoluble.
RHODIUM
as $3NaCl.RoCl_3$.</td><td>Dissolved.
IRIDIUM
as $2NaCl.IrCl_4$.</td><td>Residue;
Titanic iron,
Chrome iron,
&c.</td></tr>
</table>

The group of *platinoid metals* exhibits some very remarkable features, and it is to be regretted that this group is comparatively imperfectly known in consequence of the difficulty and expense attendant upon the purification of the metals. Its members may be arranged in two divisions, the metals in each agreeing closely in their atomic weights and specific gravities.

	Atomic weight.	Sp. gr.		Atomic weight.	Sp. gr.
Platinum . .	197.1	21.5	Palladium . .	105.7	11.5
Osmium . .	200.0	22.4	Rhodium . .	104.3	11.4
Iridium . .	192.5	22.4	Ruthenium . .	104.2	11.4.

Through osmium, this group of elements is connected with the group containing antimony, arsenic, and phosphorus, which osmium resembles in the facility with which it is oxidised, and in the volatility of the oxide formed. Palladium connects it with mercury and silver, by its solubility in nitric acid, and its insoluble cyanide and iodide.

301. DAVYUM (Da = 154) is a metal which has been found in small quantity in the ores of platinum. It is a silvery metal which dissolves in *aqua regia*. The double chloride of davyum and sodium is nearly insoluble in water and alcohol, which distinguishes davyum from the other platinum metals. Its solutions give a red colour with potassium sulphocyanide. The specific gravity of the metal is about 9.4. Davyum sulphate, obtained by heating the metal with sulphuric acid, is a yellowish red powder nearly insoluble in water. The sulphide is precipitated brown by H_2S in acid solutions. It dissolves in alkaline sulphides.

GOLD.

Au = 196.8 parts by weight.

302. The individuality of gold among metals is strongly marked, on account of its colour, its high specific gravity, 19.3, its extreme malleability and ductility, its perfect resistance to air, its high conducting power for heat and electricity, its high fusing point, 1240° C., its resistance to acids, and its rarity and consequent intrinsic value. Gold is one of those few metals which are always found in the metallic state, and is remarkable for the extent to which it is distributed, though in small quantities, over the surface of the earth. The principal supplies of this metal are derived from Australia, California, Mexico, Brazil, Peru, and the Uralian Mountains. Small quantities have been occasionally met with in our own islands, particularly at Wicklow, at Cader Idris in Wales, Leadhills in Scotland, and in Cornwall.

The mode of the occurrence of gold in the mineral kingdom resembles that of the ore of tin, for it is either found disseminated in the primitive rocks, or in alluvial deposits of sand, which appear to have been formed by the disintegration of those rocks under the continued action of torrents. In the former case, the gold is often found crystallised in cubes and octahedra, or in forms derived from these, and sometimes aggregated together in dendritic or branch-like forms. In the alluvial deposits, the gold is usually found in small scales (gold dust), but sometimes in masses of considerable size (nuggets), the rounded appearance of which indicates that they have been subjected to attrition. Australian gold is the purest, especially that from Victoria.

The extraction of the particles of gold from the alluvial sands is effected by taking advantage of the high specific gravity of the metal (19.3), which causes it to remain behind, whilst the sand, which is very much lighter (sp. gr. 2.6), is carried away by water. This washing is commonly performed by hand, in wooden or metal bowls, in which the sand is shaken up with water, and the lighter portions dexterously poured off, so as to leave the grains of gold at the bottom of the vessel. On a somewhat larger scale, the auriferous sand is washed in a *cradle* or inclined wooden trough, furnished with rockers, and with an opening at the lower end for the escape of the water. The sand is thrown on to a grating at the head of the cradle, which retains the large pebbles, whilst the sand and gold pass through, the former being washed away by a stream of water which is kept flowing through the trough.

When the gold is disseminated through masses of quartz or other rock, much labour is expended in crushing the latter before the gold can be separated. This is effected either by passing the coarse fragments between heavy rollers of hard cast-iron, or by stamping them, with wooden beams shod with iron, in troughs through which water is continually flowing.

In some cases it is found advantageous to smelt the ore by fusing it with some substance capable of uniting with the gold, and of being afterwards readily separated from it. Lead is peculiarly adapted for this purpose; the crushed ore, being mixed with a suitable proportion, either of metallic lead, or of litharge (oxide of lead) and charcoal, or even of galena (sulphide of lead), together with some lime and oxide of iron or clay, to flux the silica, is fused on the hearth of a reverberatory furnace, when the fused lead dissolves the particles of gold, and collects beneath the lighter slag. The lead is afterwards separated from the gold by cupellation (see p. 390).

In smelting the ores of gold in Hungary, the metal is concentrated by means of sulphide of iron. The ore consists of quartz and iron pyrites (disulphide of iron), containing a little gold. On fusing the crushed ore with lime, to flux the quartz, the pyrites loses half its sulphur, and becomes ferrous sulphide (FeS), which fuses and sinks below the slag, carrying with it the whole of the gold. If this product be roasted so as to convert the iron into oxide, and be then again fused with a fresh portion of the ore, the oxide of iron will flux the quartz, whilst the fresh portion of sulphide of iron will carry down the whole of the gold contained in both quantities of ore. This operation having been repeated until the sulphide of iron is rich in gold, it is fused with a certain quantity of lead, which extracts the gold and falls to the bottom. The lead is then cupelled in order to obtain the gold.

When the ores of lead, silver, or copper contain gold, it is always found to have accompanied the silver extracted from them, and is separated from it by a process to be presently noticed.

Gold is sometimes separated from the impurities remaining with it after extraction by washing, by the process of amalgamation, which consists in shaking the mixture with mercury in order to dissolve the gold-dust, and straining the liquid amalgam through chamois leather, which allows the excess of mercury to pass through, but retains the solid portion containing the gold, from which the mercury is then separated by distillation.*

In the Tyrol, this process is adopted for separating the gold from an auriferous iron pyrites, by grinding it in a mill of peculiar construction, with water and a little mercury, the latter being allowed to act upon successive portions of ore until it becomes sufficiently rich to be strained and distilled.

Chlorine water is sometimes employed to extract the gold by converting it into $AuCl_3$, the gold being afterwards precipitated from the solution by adding ferrous sulphate.

Gold, as found in nature, is generally alloyed with variable proportions of silver and copper, the separation of which is the object of the gold refiner. It may be effected by means of nitric acid, which will dissolve the silver and copper, provided that they do not bear too small a proportion to the gold. Sulphuric acid, however, being very much cheaper, is generally employed. The alloy is fused and poured into water, so as to granulate it and expose a larger surface to the action of the acid; it is then boiled with concentrated sulphuric acid (oil of vitriol), which converts the silver and the copper into sulphates, with evolution of sulphurous acid gas, whilst the gold is left untouched. In order to recover the silver from the solution of the sulphates in water, scraps of copper are introduced into it, when that metal decomposes the sulphate of silver, producing sulphate of copper, and causing the deposition of the silver in the metallic state. Finally, the sulphate of copper may be obtained from the solution by evaporation and crystallisation. This process is so effectual when the proportion of gold in an alloy is very small, that even $\frac{1}{20}$th part of this metal may be profitably extracted from 100 parts of an alloy, and much gold has been obtained in this way from old silver plate, coins, &c., which were manufactured before so perfect a process for the separation of these metals was known. On boiling old silver coins or ornaments with nitric acid, they are generally found to yield a minute proportion of gold in the form of a purple powder. But this plan of separation is not so successful when the alloy contains a very large quantity of gold, for the latter metal protects the copper and silver from the solvent action of the acid. Thus, if the alloy contains more than $\frac{1}{5}$th of its weight of gold, it is customary to fuse it with a quantity of silver, so as to reduce the proportion of gold below that point before boiling it with the acid. Again, if the alloy contains a large quantity of copper, it is found expedient to remove a great deal of this metal in the form of oxide by heating the alloy in a current of air.

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* A small quantity of sodium dissolved in the mercury has been found very materially to facilitate the amalgamation of gold and silver ores, apparently because the amalgam of sodium is more highly electro-positive than mercury, in relation to the gold.

Gold which is brittle and unfit for coining, in consequence of the presence of small quantities of foreign metals, is sometimes refined by melting it with oxide of copper or with a mixture of nitre and borax, when the foreign metals, with the exception of silver, are oxidised and dissolved in the slag. Another process consists in throwing some corrosive sublimate (mercuric chloride) into the melting pot, and stirring it up with the metal, when its vapour converts the metallic impurities into chlorides, which are volatilised. An excellent method, devised by F. B. Miller of Sydney, consists in fusing the gold with a little borax, and passing chlorine gas into it through a clay tube. Antimony, arsenic, &c., are carried off as chlorides, whilst the silver, also converted into chloride, rises to the surface of the gold in a fused state, afterwards solidifying into a cake, which is reduced to the metallic state by placing it between plates of wrought-iron and immersing it in diluted sulphuric acid.

Pure gold, like pure silver, is too soft to resist the wear to which it is subjected in its ordinary uses, and it is therefore alloyed for coinage in this country with $\frac{1}{12}$th of its weight of copper, so that gold coin contains 1 part of copper and 11 parts of gold. The gold used for articles of jewellery is alloyed with variable proportions of copper and silver. The alloy of copper and gold is much redder than pure gold.

The English sovereign contains 91.67 per cent. of gold and 8.33 per cent. of copper. Its sp. gr. is 17.157, and its weight is 123.274 grains. The Australian sovereign contains silver in place of copper, and is lighter in colour than pure gold.

The degree of purity of gold is generally expressed by quoting it as of so many carats fine. Thus, pure gold is said to be 24 carats fine; English standard gold 22 carats fine, that is, contains 22 carats of gold out of the 24. Gold of 18 carats fine would contain 18 parts of gold out of the 24, or $\frac{3}{4}$ths of its weight of gold. The other legal standards are 15, 12, and 9 carat gold. The *fineness* sometimes refers to the quantity of gold in 1000 parts of the alloy; thus, English coin has a fineness of 916.7, German and American coin, of 900.

In order to impart to gold ornaments the appearance of pure gold, they are heated till the copper in the outer layer is oxidised, and then dipped into nitric or sulphuric acid, which dissolves the copper oxide and leaves a film of pure gold.

Pure gold is easily prepared from standard or jeweller's gold, by dissolving it in hydrochloric acid mixed with one-fourth of its volume of nitric acid, evaporating the solution to a small bulk to expel excess of acid, diluting with a considerable quantity of water, filtering from the separated silver chloride, and adding a solution of green sulphate of iron, when the gold is precipitated as a dark purple-powder, which may be collected on a filter, well washed, dried, and fused in a small French clay crucible with a little borax, the crucible having been previously dipped in a hot saturated solution of borax, and dried, to prevent adhesion of the globules of gold. The action of the ferrous sulphate upon the trichloride of gold is explained by the equation—

$$2AuCl_3 + 6Fe_2SO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

The gold precipitated by ferrous sulphate appears, under the microscope, in cubical crystals.

By employing oxalic acid instead of ferrous sulphate, and heating the solution, the gold is precipitated in a spongy state, and becomes a coherent lustrous mass under pressure. The metal is employed in this form by dentists.

When standard gold is being dissolved in *aqua regia*, it sometimes becomes coated with a film of silver chloride which stops the action of the acid; the liquid must then be poured off, the metal washed, and treated with ammonia, which dissolves the silver chloride; the ammonia must then be washed away before the metal is replaced in the acid. In the case of jeweller's gold, it is advisable to extract as much silver and copper as possible by boiling it with nitric acid, before attempting to dissolve the gold. Gold lace should be incinerated to get rid of the cotton before being treated with acid.

The genuineness of gold trinkets, &c., is generally tested by touching them with nitric acid, which attacks them if they contain a very considerable proportion of copper, producing a green stain, but this test is evidently useless if the surface be gilt. The weight is, of course, a good criterion in practised hands, but even these have been deceived by bars of platinum covered with gold. The specific gravity may be taken in doubtful cases; that of sovereign gold is 17.157.

In *assaying gold*, the metal is wrapped in a piece of thin paper together with about three times its weight of pure silver, and added to twelve times its weight of pure lead fused in a bone-ash *cupel* (see page 391) placed in a muffle (or exposed to a strong oxidising blowpipe flame), when the lead and copper are oxidised, and the fused oxide of lead dissolves that of copper, both being absorbed by the cupel. When the metallic button no longer diminishes in size, it is allowed to cool, hammered into a flat disc which is annealed by being heated to redness, and rolled out to a thin plate, so that it may be rolled up by the thumb and finger into a *cornette*, which is boiled with nitric acid (sp. gr. 1.18) to extract the silver; the remaining gold is washed with distilled water, and boiled with nitric acid of sp. gr. 1.28, to extract the last traces of silver, after which it is again washed, heated to redness in a small crucible, and weighed.

The stronger nitric acid could not be used at first, since it would be likely to break the cornette into fragments which could not be so readily washed without loss. The addition of the three parts of silver (*quartation*) is made in order to divide the alloy, and permit the easy extraction of the silver by nitric acid, which cannot be effected when the gold predominates.

303. The physical characters of gold render it very conspicuous among the metals; it is the heaviest of the metals in common use, with the exception of platinum, its specific gravity being 19.3. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper is passed between rollers which extend it into the form of a riband; this is cut up into squares, which are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed upon each other form a pile of only 1 inch high. These leaves will allow light to pass through them, and always

appear green or blue when held up to the light, though they exhibit the ordinary colour of gold by reflected light. If a gold leaf adhering to a glass plate be heated to nearly the boiling point of oil for some time, it becomes nearly transparent and invisible by transmitted light, though still showing the colour of gold by reflected light; if it be pressed with a moderately hard body, it again transmits a green light. When gold wire or leaf is deflagrated by electricity on a glass plate, the finely divided metal transmits ruby, violet, and green light, according to its thickness, though it has the golden colour by reflected light. On heating these deposits to dull redness on the glass, they all change to the ruby colour while still golden by reflection. Pressure with a hard body changes the colour of the transmitted light from red to green. A solution of gold trichloride, containing 0.6 grain of gold in a quart, if shaken with a little solution of phosphorus in ether, in a chemically clean bottle, gives a ruby-red liquid in which the reflected colour of gold may be seen by bringing the solar rays to a focus in the liquid by a convex lens. This liquid will continue to deposit fine particles of gold for many months. The first deposits are blue by transmitted light, and the last are ruby. The supernatant liquid is eventually colourless. If a little sodium chloride be added to the ruby liquid, it transmits a blue light, and the gold which has remained suspended for six months may be deposited in a few hours. By using a filter arranged so that the liquid is passed through the paper in a *radial* instead of an *axial* direction as is usual, the particles of gold, which pass through in ordinary axial filtration, may be collected on the paper, having the various colours, and leaving the liquid colourless. These colours of finely divided gold are taken advantage of in painting upon porcelain, and the well-known magnificent ruby-red glass owes its colour to the same cause. $\frac{1}{100}$th of a grain of gold is capable of imparting a deep rose colour to a cubic inch of fluid.

The extreme ductility of gold is exemplified in the manufacture of gold thread for embroidery, in which a cylinder of silver having been covered with gold leaf, it is drawn through a wire-drawing plate and reduced to the thinness of a hair; in this way 6 ounces of gold are drawn into a cylinder two hundred miles in length. Although fusing at somewhat above the melting point of copper, gold is seldom cast, on account of its great contraction during solidification.

Gold is not even affected to the same extent as silver by exposure to the atmosphere, for sulphuretted hydrogen has no action upon it, and hence no metal is so well adapted for coating surfaces which are required to preserve their lustre.

The gold is sometimes applied to the surfaces of metals in the form of an amalgam, the mercury being afterwards driven off by heat. Metals may also be gilt by means of a boiling solution prepared by dissolving gold in *aqua regia*, and adding an excess of bicarbonate of potash or of soda. But the most elegant process of gilding is that of electro-gilding, in which the object to be gilt is connected by a wire with the zinc end of the galvanic battery, and immersed in a solution of cyanide of gold in cyanide of potassium, in which is also placed a gold plate connected with the copper end of the battery, and intended, by gradually dissolving, to replace the gold abstracted from the solution at the negative pole.

A gold crucible is very useful in the laboratory for effecting the fusion of substances with caustic alkalies, which would corrode a platinum crucible. The only single acid which attacks gold is selenic, H_2SeO_4, which the gold reduces to selenious acid, H_2SeO_3. A mixture of hydrochloric with one-third of its volume of nitric acid is usually employed for dissolving gold. It is also dissolved by a mixture of sulphuric acid with a little nitric, the latter becoming reduced to nitrous acid, which precipitates the gold again in the metallic state on pouring the solution into a large volume of water.

Fused caustic alkalies are not without action on gold, but they attack platinum more strongly.

304. OXIDES OF GOLD.—Two compounds of gold with oxygen have been obtained, Au_2O and Au_2O_3, but neither of them is of any great practical importance.

Aurous oxide, Au_2O, obtained by decomposing aurous chloride with potash, is a violet coloured powder which is decomposed by hydrochloric acid—

$$3Au_2O + 6HCl = 2AuCl_3 + 3H_2O + Au_4.$$

Auric oxide, Au_2O_3, is obtained by gently heating *auric hydrate*, $Au(HO)_3$. This is prepared by heating a weak solution of auric chloride with excess of potash, and adding sodium sulphate, when auric hydrate is precipitated, of a brown colour like ferric hydrate. It is very unstable, evolving oxygen when exposed to light. Nitric acid dissolves it, and it is reprecipitated by water. It dissolves in potash, and the solution yields crystals of *potassium aurate*, $KAuO_2.3Aq$.

When precipitated gold is acted on by chlorine gas, it yields *auroso-auric chloride*, $AuCl.AuCl_3$, a dark red hard substance decomposed by water into $AuCl$ and $AuCl_3$, or *auric chloride*, which may also be obtained by dissolving gold in hydrochloric acid with one-fourth of its volume of nitric acid, and evaporating on a water bath to a small bulk; on cooling, yellow prismatic crystals of a compound of the trichloride with hydrochloric acid ($AuCl_3.HCl.4Aq$) are deposited, from which the hydrochloric acid may be expelled by a gentle heat (not exceeding 120° C.), when the trichloride forms red-brown deliquescent crystals of $AuCl_3.2Aq$, dissolving very readily in water, giving a bright yellow solution which stains the skin and other organic matter purple when exposed to light, depositing finely divided gold. Almost every substance capable of combining with oxygen reduces the gold to the metallic state. The inside of a perfectly clean flask or tube may be covered with a film of metallic gold by a dilute solution of the trichloride mixed with citric acid and ammonia, and gently heated. The facility with which it deposits metallic gold, and the resistance of the deposited metal to atmospheric action, has rendered trichloride of gold very useful in photography. Alcohol and ether readily dissolve the trichloride, the latter being able to extract it from its aqueous solution. Red crystals of trichloride of gold are sublimed when thin gold foil is gently heated in a current of chlorine. Trichloride of gold (like platinic chloride) forms crystallisable compounds with the alkaline chlorides and with the hydrochlorates of organic bases, and affords great help to the chemist in defining these last. *Aurochloride of sodium* forms reddish-yellow prismatic crystals ($NaCl.AuCl_3.2Aq$), which are sometimes sold for photographic purposes.

Protochloride of gold, or *aurous chloride* ($AuCl$), is obtained by gently heating the trichloride, when it fuses and is decomposed at 177° C., leaving the protochloride, which is reduced to metallic gold at about

205° C. Aurous chloride is sparingly soluble in water, and of a pale yellow colour. Boiling water decomposes it into metallic gold and the trichloride.

Fulminating gold is obtained as a buff precipitate when ammonia is added to solution of auric chloride; its composition is not well established, but appears to be $Au_2O_3.4NH_3$ or $2(NH_3.NAu''').3H_2O$. It explodes violently when gently heated.

The *Sel d'or* of the photographer is a hyposulphite (thiosulphate) of gold and sodium, $Au_2S_2O_3.3Na_2S_2O_3.4Aq$, which is obtained in fine white needles by pouring a solution of 1 part of auric chloride into a solution of 3 parts of sodium hyposulphite, and adding alcohol, in which the double salt is insoluble. Its formation may be explained by the equation $8Na_2S_2O_3 + 2AuCl_3 = Au_2S_2O_3.3Na_2S_2O_3 + 6NaCl + 2Na_2S_4O_6$. It is doubtful whether the above formula represents the true constitution of this salt, for it is not decomposed by acids in the same manner as ordinary thiosulphates.* Nitric acid causes the whole of the gold to separate in the metallic state.

Purple of Cassius, which is employed for imparting a rich red colour to glass and porcelain, is a compound of gold, tin, and oxygen, which are believed to be grouped according to the formula $Au_2SnO_3.Sn.SnO_3.4Aq$.† It may be prepared by adding stannous chloride to a mixture of stannic chloride and auric chloride; 7 parts of gold are dissolved in *aqua regia* and mixed with 2 parts of tin also dissolved in *aqua regia*; this solution is largely diluted with water, and a weak solution of 1 part of tin in hydrochloric acid is added, drop by drop, till a fine purple colour is produced. The purple of Cassius remains suspended in water in a very fine state of division, but subsides gradually, especially if some saline solution be added, as a purple powder. The fresh precipitate dissolves in ammonia, but the purple solution is decomposed by exposure to light, becoming blue, and finally colourless, metallic gold being precipitated, and stannic oxide left in solution.

The SULPHIDES OF GOLD are not thoroughly known. Gold does not combine directly with sulphur, but if it be heated with sulphur and alkaline sulphides, it forms soluble compounds. In this way, *sodium aurosulphide*, $NaAuS.4Aq$, may be obtained in colourless prisms soluble in alcohol. When H_2S is passed into solution of $AuCl_3$, a black precipitate of $Au_2S.Au_2S_3$ or Au_2S_2 is obtained; $2AuCl_3 + 3H_2S = Au_2S_2 + S + 6HCl$. The precipitate is soluble in alkaline sulphides. The precipitated sulphide of gold is not dissolved by the acids, with the exception of *aqua regia*. Nitric acid oxidises the sulphur, leaving metallic gold. When hydrosulphuric acid is added to a boiling solution of auric chloride, the metal itself is precipitated—

$$8AuCl_3 + 3H_2S + 12H_2O = Au_8 + 24HCl + 3H_2SO_4.$$

A yellowish-grey brittle *arsenide of gold* ($AuAs_2$) has been found in quartz in Australia.

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* It appears to be *sodium aurothiosulphate*, $Na_3AuS_4O_6.2Aq$, which is supported by the preparation of a corresponding barium salt and by decomposing this with sulphuric acid, when *aurothiosulphuric acid*, $H_3AuS_4O_6$, is obtained.

† Debray asserts that it is merely a mixture of precipitated gold and stannic hydrate.

DETERMINATION OF ATOMIC WEIGHTS.

304*a*. Since the numbers affixed to the elements, as representing their relative atomic weights are of the first importance, it may be well to conclude the history of individual elements with a brief review of the considerations by which their atomic weights have been fixed at their present values.

(1) The atomic weight of H is 1, because it is taken as the standard by common agreement among chemists.

(2) Those elements which can be measured in the state of gas have for their atomic weight that quantity (in grammes) which, in the state of gas, occupies the same volume as 1 gramme of hydrogen at the same temperature and pressure. This fixes the atomic weights of O, N, Cl, Br, I, S, Se, K.

(3) Those elements which form compounds capable of being measured in the state of gas have, for their atomic weight, the smallest weight (in grammes) of the element which can be found in 22.32 litres of any of their gaseous compounds, at 0° C. and 760 mm. Bar. This fixes the atomic weights of Sb, As, Bi, B, C, F, Hg, P, Si, and Sn, and confirms those of O, N, Cl, Br, I, S, and Se, fixed by consideration 2.

(4) Those elements whose specific heats in the solid state can be determined, have for their atomic weight that number which is obtained by dividing 6.4 by the specific heat. This fixes the atomic weights of nearly all the solid elements, and is of especial value in the following cases, which could not be decided by the other methods:—Al, Cd, Co, Cu, Au, Fe, Pb, Mg, Mn, Hg, Ni, P, Pt, Ag, Na, Zn.

(The *specific heat* is the quantity of heat required to raise one part by weight of any body through 1° in temperature. The *atomic heats* are the quantities of heat required to raise the atomic weights of bodies through 1°.)

The atomic heats of the solid elements are all expressed by the same number, viz., 6.4. Hence, if this number be divided by the specific heat, the quotient will be the atomic weight. Experimentally, the atomic weight may be determined by ascertaining what weight of the substance contains the same amount of heat as is contained in 108 parts by weight of silver at the same temperature.

(5) The atomic weight of an element is generally a multiple of its equivalent weight by 1, 2, 3, or 4; the equivalent weight being that which is found by experiment to be exchangeable for 1 gramme of hydrogen.

(6) When any doubt remains, the chemical analogies of the element with some other element of known atomic weight are taken into consideration.

ON SOME OF THE

USEFUL APPLICATIONS OF CHEMICAL PRINCIPLES NOT HITHERTO MENTIONED.

CHEMICAL PRINCIPLES OF THE MANUFACTURE OF GLASS.

305. Glass is defined chemically to be a mixture of two or more silicates, one of which is a silicate of an alkali-metal, the other being a silicate of calcium, barium, iron, lead, or zinc.

If silica be fused with an equal weight of carbonate of potassium or sodium, a transparent glassy mass is obtained, but this is slowly dissolved by water, and would therefore be incapable of resisting the action of the weather; if a small proportion of lime or baryta, or of the oxides of iron, lead, or zinc, be added, the glass becomes far less easily affected by atmospheric influences.

The most valuable property of glass, after its transparency and permanence, is that of assuming a viscid or plastic consistency when fused, which allows it to be so easily fashioned into the various shapes required for use or ornament.

The composition of glass is varied according to the particular purpose for which it is intended, the materials selected being fused in large clay crucibles placed in reverberatory furnaces, and heated by a coal fire or in a gas-furnace.

Ordinary *window glass* is essentially composed of sodium silicate and calcium silicate, containing one molecule (13.3 per cent.) of soda, one molecule (12.9 per cent.) of lime, and five molecules (69.1 per cent.) of silica; it also usually contains a little alumina. This variety of glass is manufactured by fusing 100 parts of sand with about 35 parts of chalk and 35 parts of soda-ash: a considerable quantity of broken window glass is always fused up at the same time. Of course, carbonic acid gas is expelled from the chalk and the sodium carbonate in the gaseous state; and in order that this may not cause the contents of the crucible to froth over during the fusion, the materials are first *fritted* together, as it is termed, at a temperature insufficient to liquefy them, when the carbonic acid gas is evolved gradually, and the fusion afterwards takes place without effervescence.

Occasionally, sodium sulphate is employed instead of the carbonate, when it is usual to add a small proportion of charcoal in order to facilitate the decomposition of the sulphate by removing part of its oxygen ($Na_2SO_4 + SiO_2 + C = Na_2SiO_3 + SO_2 + CO$). Before the glass is worked into sheets, it is allowed to remain at rest for some time in the fused state, so that the air-bubbles may escape, and the *glass-gall* or scum (consisting chiefly of sodium sulphate and sodium chloride), which rises to the surface, is removed.

Plate glass is also chiefly a silicate of sodium and calcium, but it contains, in addition, a considerable quantity of silicate of potassium (74 per cent. of SiO_2, 12 of Na_2O, 5.5 of K_2O, and 5.5 of CaO). The purest white sand is selected, and great care is taken to exclude impurities.

Crown glass, used for optical purposes, contains no sodium, since that metal has the property of imparting a greenish tint to glass, which is not the case with potassium. This variety of glass, therefore, is prepared by fusing sand with potassium carbonate and chalk in such proportions that the glass may contain 1 molecule (22 per cent.) of K_2O, 1 molecule (12.5 per cent.) of CaO, and 4 molecules (62 per cent.) of SiO_2.

The glass of which *wine bottles* are made is of a much cheaper and commoner description, consisting chiefly of calcium silicate, but containing, in addition, small quantities of the silicates of sodium, of aluminium, and of iron, to the last of which it owes its dark colour. It is made of the coarsest materials, such as common red sand (containing iron and alumina), soap-maker's waste (containing lime and small quantities of alkali), refuse lime from the gas-works, clay, and a very small proportion of rock-salt.

Flint glass, which is used for table glass and for ornamental purposes, is a double silicate of potassium and lead, containing one molecule (13.67 per cent.) of K_2O, one molecule (33.28 per cent.) of PbO, and six molecules (51.93 per cent.) of SiO_2. It is prepared by fusing 300 parts of the purest white sand with 200 parts of minium (red oxide of lead), 100 parts of refined pearl-ash, and 30 parts of nitre. The fusion is effected in crucibles covered in at the top to prevent the access of the flame, which would reduce a portion of the lead to the metallic state. The nitre is added in order to oxidise any accidental impurities which might reduce the lead.

The presence of the lead in glass very much increases its fusibility, and renders it much softer, so that it may be more easily cut into ornamental forms; it also greatly increases its lustre and beauty.

Barium has also the effect of increasing the fusibility of glass, and zinc, like lead, increases its brilliancy and refracting power, on which account it is employed in some kinds of glass for optical purposes. Glass of this description is also made by substituting boric oxide for a portion of the silica.

Some varieties of glass, if heated nearly to their melting point, and allowed to cool slowly, become converted into an opaque very hard mass resembling porcelain (*Réaumur's porcelain*). This change, which is known as *devitrification*, is due to the crystallisation of the silicates contained in the mass, and, by again fusing it, the glass may be restored to its original transparent condition.

Toughened glass is made by heating the glass vessel to its softening point, immersing it in a bath of oil or steam at 200° C., and cooling it quickly. This treatment hardens it, increases its specific gravity, and renders it less brittle externally, but puts the inner portion in a state of tension, so that it sometimes breaks up spontaneously.

In producing *coloured glass*, advantage is taken of its property of dissolving many metallic oxides with production of peculiar colours. It has been mentioned above that bottle glass owes its green colour to the presence of iron; and since this metal is generally found in small quantity in sand, and even in chalk, it occasionally happens that a glass which is required to be perfectly colourless turns out to have a slight green tinge. In order to remove this, a small quantity of some oxidising agent is usually added, in order to convert the ferrous oxide into ferric oxide, which does not impart any colour when present in minute proportion. A little nitre is sometimes added for this purpose, or some white arsenic, which yields its oxygen to the ferrous oxide, and escapes in the form of vapour of arsenic; red oxide of lead (Pb_3O_4) may also be employed, and is reduced to oxide of lead (PbO), which remains in the glass. Manganese dioxide is often added as an oxidising agent, being reduced to the state of manganous oxide (MnO), which does not colour the glass; but care is then taken not to add too much of the dioxide, for a very minute quantity of this substance imparts a beautiful amethyst purple colour to glass.

Suboxide of copper is used to produce a red glass, and the finest ruby glass is obtained, as already mentioned at page 429, by the addition of a little gold. The oxides of antimony impart a yellow colour to glass; a peculiar brown-yellow shade is given by charcoal in a fine state of division, and sesquioxide of uranium produces a fine greenish-yellow glass. Green glass is coloured either by oxide of copper or sesquioxide of chromium, whilst oxide of cobalt gives a magnificent blue colour. For black glass a mixture of the oxides of cobalt and manganese is employed. The white enamel glass is a flint glass, containing about 10 per cent. of binoxide of tin. Bone-ash is also used to impart this appearance to glass. The *irisation* of glass, giving it the tints of mother-of-pearl, is effected by corroding its surface with hydrochloric acid of 15 per cent. strength, under heat and pressure.

Kryolite is employed in making *opal-glass* containing 64 per cent. of silica, 17 of alumina, 16 of lead oxide, and 3 of potash.

CHEMISTRY OF THE MANUFACTURE OF POTTERY AND PORCELAIN.

306. The manufacture of pottery obviously belongs to an earlier period of civilisation than that of glass, since the raw material, clay, would at once suggest, by its plastic properties, the possibility of working it into useful vessels, and the application of heat would naturally be had recourse to in order to dry and harden it. Indeed, at the first glance, it would appear that this manufacture, unlike that of glass, did not involve the application of chemical principles, but consisted simply in fashioning the clay by mere mechanical dexterity into the required form. It is found, however, at the outset, that the name of *clay* is applied to a large class of minerals, differing very considerably in composition, and possessing in common the two characteristic features of plasticity and a predominance of aluminium silicate.

It has already been stated (page 298) that *kaolin* is a hydrated aluminium silicate, and it is from this material that the best variety of porcelain is made. This clay is eminently plastic, and can therefore be readily moulded, but when baked it shrinks very much, so that the vessels made from it lose their shape and often crack in the kiln. In order to prevent this, the clay is mixed with a certain proportion of sand, chalk, bone-ash, or heavy-spar; but another difficulty is thus introduced, for these substances diminish the tenacity of the clay, and would thus render the vessels brittle. A further addition must therefore be made of some substance which fuses at the temperature employed in baking the ware, and thus serves as a cement to bind the unfused particles of clay, &c., into a compact mass. Felspar (silicate of aluminium and potassium) answers this purpose; or carbonate of potassium or of sodium is sometimes added, to convert a portion of the silica into a fusible alkaline silicate. With a mixture of clay with sand and felspar (or some substitutes), a vessel may be moulded which will preserve its shape and tenacity when baked, but it will be easily pervious to water, and thus quite unfit for ordinary use. It has, therefore, to be waterproofed by the application of some easily fusible material, which shall either form a glaze over the surface, or shall become incorporated with the body of the ware, and the vessel is then fit for all its uses. Handles and ornaments in relief are moulded separately, and fixed on the ware before baking, and coloured designs are transferred from paper to the porous ware before glazing.

The manufacture of *Sèvres porcelain* is one of the most perfect examples of this art. The purest materials are selected in the following proportions:—Kaolin (porcelain clay), 62 parts; chalk, 4 parts; sand, 17 parts; felspar, 17 parts. These materials are ground up with water before being mixed, and the coarser particles are allowed to subside; the creamy fluids containing the finer particles in suspension are then mixed in the proper proportions, and allowed to settle; the paste deposited at the bottom is drained, thoroughly kneaded, and stored away for some months in a damp place, by which its texture is considerably improved, and any organic matter which it contains becomes oxidised and removed, the oxidation being effected partly by the sulphates present, which become reduced to sulphides. It is then moulded into the required forms, and dried by simple exposure to the air. The vessels are packed in cylindrical cases of a very refractory clay, which are arranged in a furnace or kiln of peculiar construction, and very gradually but strongly heated by the flame of a wood fire. When sufficiently baked, the *biscuit* porcelain has to be glazed, and great care is taken that the glaze may possess the same expansibility by heat as the ware itself, for otherwise it would crack in all directions as the glazed ware cooled. The glaze employed at Sèvres is a mixture of felspar and quartz very finely ground, and suspended in water, to which a little vinegar is added to prevent the glaze from subsiding too rapidly. When the porous ware is dipped into this mixture, it absorbs the water, and retains a thin coating of the mixture of quartz and felspar upon its surface. It is now baked a second time, when the glaze fuses, partly penetrating the ware, partly remaining as a varnish upon the surface.

When the ware is required to have some uniform colour, a mineral pigment capable of resisting very high temperatures is mixed with the glaze; but coloured designs are painted upon the ware after glazing, the ware being then baked a third time, in order to fix the colours. These colours are glasses coloured with metallic oxides, and ground up with oil of turpentine, so that they may be painted in the ordinary way upon the surface of the ware; when the latter is again heated in the kiln, the coloured glass fuses, and thus contracts a firm adhesion with the ware.

Gold is applied either in the form of precipitated metallic gold, or of fulminating gold, being ground up in either case with oil of turpentine, burnt in, and burnished.

English porcelain is made from Cornish clay mixed with ground flints, burnt bones, and sometimes a little sodium carbonate, borax, and binoxide of tin, the last improving the colour of the ware. It is glazed with a mixture of Cornish stone (consisting of quartz and felspar), flint, chalk, borax, and sometimes white lead to increase its fusibility.

Stone-ware is made from less pure materials, and is covered with a glaze of sodium silicate, in a very simple manner, by a process known as *salt-glazing*. The ware is coated with a thin film of sand by dipping it in a mixture of fine sand and water, and is then intensely heated in a kiln into which a quantity of damp salt is presently thrown. The water is decomposed, its hydrogen taking the chlorine of the salt to form hydrochloric acid, and its oyxgen converting the sodium into soda, which combines with the sand to form sodium silicate; this fuses into a glass upon the surface of the ware.

Pipkins, and similar earthenware vessels, are made of common clay mixed with a certain proportion of marl and of sand. They are glazed with a mixture of 4 or 5 parts of clay with 6 or 7 parts of litharge. The colour of this ware is due to the presence of ferric oxide.

Bricks and tiles are also made from common clay mixed, if necessary, with sand. These are very often grey, or blue, or yellow, before baking, and become red under the action of heat, since the iron, which is originally present as carbonate ($FeCO_3$), becomes converted into the red peroxide (Fe_2O_3) by the atmospheric oxygen.

The impure varieties of clay fuse much more easily than pure clay, so that, for the manufacture of the refractory bricks for lining furnaces, of glass-pots, crucibles for making cast-steel, &c., a pure clay is employed, to which a certain quantity of broken pots of the same material is added, to prevent the articles from shrinking whilst being dried.

Dinas firebricks are made from a peculiar siliceous material found in the Vale of Neath, and containing alumina with about 98 per cent. of silica. The ground rock is mixed with 1 per cent. of lime and a little water before moulding. These bricks are expanded by heat, whilst ordinary firebricks contract.

Blue bricks are glazed by sprinkling with *iron scurf*, a mixture of particles of stone and iron produced by the wear of the siliceous grindstones employed in grinding gun-barrels, &c. When the bricks are fired, a glaze of silicate of iron is formed upon them.

CHEMISTRY OF BUILDING MATERIALS.

307. Chemical principles would lead to the selection of pure silica (quartz, rock-crystal) as the most durable of building materials, since it is not acted on by any of the substances likely to be present in the atmosphere; but even if it could be obtained in sufficiently large masses for the purpose, its great hardness presents an obstacle to its being hewn into the required forms. Of the building stones actually employed, *granite*, *basalt*, and *porphyry* are the most lasting, on account

of their capability of resisting for a great length of time the action of water and of atmospheric carbonic acid; but their hardness makes them so difficult to work, as to prevent their employment except for the construction of pavements, bridges, &c., where the work is massive and straightforward, and much resistance to wear and tear is required. The *millstone grit* is also a very durable stone, consisting chiefly of silica, and employed for the foundations of houses. *Freestone* is a term applied to any stone which is soft enough to be wrought with hammer and chisel, or cut with a saw; it includes the different varieties of sandstone and limestone. The sandstones consist of grains of sand cemented together by clay or limestone. The *Yorkshire flags* employed for paving are siliceous stones of this description. The *Craigleith sandstone*, which is one of the freestones used in London, contains about 98 per cent. of silica, together with some calcium carbonate.

The building stones in most general use are the different varieties of calcium carbonate. The durability of these is in proportion to their compact structure; thus *marble*, being the most compact, has been found to resist for many centuries the action of the atmosphere, whilst the more porous limestones are corroded at the surface in a very short time. *Portland stone*, of which St. Paul's and Somerset House are built, and *Bath stone*, are among the most durable of these; but they are all slowly corroded by exposure to the atmosphere. The chief cause of this corrosion appears to be the mechanical disintegration caused by the expansion, in freezing, of the water absorbed in the pores of the stone. In order to determine the relative extent to which different stones are liable to be disintegrated by frost, a test has been devised, which consists in soaking the stone repeatedly in a saturated solution of sodium sulphate and allowing it to dry, when the crystallisation of the salt disintegrates the stone, as freezing water would, so that if the particles detached from the surface be collected and weighed, a numerical expression for the resistance of the material will be obtained (*Brard's test*). *Magnesian limestones* (carbonate of calcium with carbonate of magnesium) are much valued for ornamental architecture, on account of the ease with which they may be carved, and are said to be more durable in proportion as they approach the composition expressed by the formula $CaCO_3.MgCO_3$.* The magnesian limestone from Bolsover Moor, of which the Houses of Parliament are built, contains 50 per cent. of calcium carbonate, 40 of magnesium carbonate, with some silica and alumina.

It is probable that a slow corrosion of the surface of limestone is effected by the carbonic acid continually deposited in aqueous solution from the air; and it is certain that in the atmosphere of towns the limestone is attacked by the sulphuric acid which results from the combustion of coal and the operations of chemical works. The Houses of Parliament have suffered severely, probably from this cause. Many processes have been recommended for the preservation of building stones, such as waterproofing them by the application of oily and resinous substances, and coating or impregnating them with solution of soluble glass and similar matters; but none seems yet to have been thoroughly tested by practical experience.

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* Any excess of calcium carbonate above that required by this formula may be dissolved out by treating the powdered magnesian limestone with weak acetic acid.

Purbeck, *Ancaster*, and *Caen stones* are well-known limestones employed for building.

The *mortar* employed for building is composed of 1 part of freshly slaked lime and 2 or 3 parts of sand intimately mixed with enough water to form an uniform paste. The hardening of such a composition appears to be due, in the first instance, to the absorption of carbonic acid from the air, by which a portion of the lime is converted into calcium carbonate, and this, uniting with the unaltered calcium hydrate, forms a solid layer, adhering closely to the two surfaces of brick or stone, which it cements together. In the course of time the lime would act upon the silica, producing calcium silicate, and this chemical action would render the adhesion more perfect. The chief use of the sand here, as in the manufacture of pottery (page 436), is to prevent excessive shrinking during the drying of the mortar.

In constructions which are exposed to the action of water, mortars of peculiar composition are employed. These *hydraulic mortars*, or *cements*, as they are termed, are prepared by calcining mixtures of calcium carbonate with from 10 to 30 per cent. of clay, when carbonic acid gas is expelled, and the lime combines with a portion of the silica from the clay, producing calcium silicate, and probably also, with the alumina, forming calcium aluminate. When the calcined mass is ground to powder and mixed with water, the silicates of aluminium and calcium, and the calcium aluminate, unite to form hydrated double silicates and aluminates, upon which water has no action. Roman cement is prepared by calcining a limestone containing about 20 per cent. of clay, and hardens in a very short time after mixing with water.

For Portland cement (so called from its resembling Portland stone) a mixture of river mud (chiefly clay) and limestone is calcined at a very high temperature.

Concrete is a mixture of hydraulic cement with small gravel. A specimen of this material from a very ancient Phœnician temple was as hard as rock, and contained nearly 30 per cent. of pebbles.

Scott's cement was prepared by passing air containing a small quantity of sulphurous acid gas, evolved from burning sulphur, over quicklime heated to dull redness. The setting of this cement appears due to the presence of a small proportion of calcium sulphate very intimately mixed with the quicklime. The mixture of these substances yields the cement by a less circuitous process.

GUNPOWDER.

308. Gunpowder is a very intimate mixture of saltpetre (nitre or potassium nitrate), sulphur, and charcoal, which do not act upon each other at the ordinary temperature, but, when heated together, arrange themselves into new forms, evolving a very large amount of gas.

In order to manufacture gunpowder capable of producing the greatest possible effect, great attention is requisite to the purity of the ingredients, the process of mixing, and the form ultimately given to the finished powder.

CHEMISTRY OF THE INGREDIENTS OF GUNPOWDER.—SALTPETRE.—*Potassium nitrate* (KNO_3), *nitre*, or *saltpetre* is found in some parts of India, especially in Bengal and Oude, where it sometimes appears as a white incrustation on the surface of the soil, and is sometimes mixed with it to some depth. The nitre is extracted from the earth by treating it with water, and the solution is evaporated, at first by the heat of the sun, and afterwards by artificial heat, when the impure crystals are obtained, which are packed in bags and sent to this country as *grough* (or impure) saltpetre. It contains a quantity of extraneous matter varying from 1 to 10 per cent., and consisting of the chlorides of potassium and sodium, sulphates of potassium, sodium, and calcium, vegetable matter from the soil, sand, and moisture. The number representing the weight of impurity present is usually termed the *refraction* of the nitre, in allusion to the old method of estimating it by casting the melted nitre into a cake and examining its fracture, the appearance of which varies according to the amount of foreign matter present.

Peruvian or *Chili saltpetre* is the *nitrate of sodium* ($NaNO_3$) found in Peru and Chili in beds beneath the surface soil. It is often spoken of as *cubical saltpetre*, since it crystallises in rhombohedra, easily mistaken for cubes, whilst *prismatic saltpetre*, nitrate of potassium, crystallises in six-sided prisms. Sodium nitrate cannot be substituted for potassium nitrate as an ingredient of gunpowder, since it attracts moisture from the air, becoming damp, and is less powerful in its oxidising action upon combustible bodies at a high temperature. The Peruvian saltpetre, however, forms a very important source from which to prepare the potassium nitrate for gunpowder, since it is easily converted into this salt by double decomposition with potassium chloride. The latter salt is now imported in so large a quantity from the salt-mines of Stassfurt (p. 256) that it enables sodium nitrate to be very cheaply converted into potassium nitrate, and renders Indian saltpetre of less importance to the manufacturer of gunpowder.

In order to understand the production of saltpetre by the decomposition of sodium nitrate with potassium chloride, it is necessary to be acquainted with the solubility of those salts and of the salts produced by their mutual decomposition.

100 parts of boiling water dissolve		100 parts of cold water dissolve	
218 parts of	sodium nitrate	50 parts of	sodium nitrate
53 ,,	potassium chloride	33 ,,	potassium chloride
200 ,,	potassium nitrate	30 ,,	potassium nitrate
37 ,,	sodium chloride	36 ,,	sodium chloride

It is a general rule that when two salts in solution are mixed, which are capable of forming, by exchange of their metals, a salt which is less soluble in the liquid, that salt will be produced and separated.

Thus, when sodium nitrate and potassium chloride are mixed, and the solution boiled down, sodium chloride is deposited, and potassium nitrate remains in the boiling liquid; $NaNO_3 + KCl = KNO_3 + NaCl$. When this is allowed to cool, the greater part of the potassium nitrate crystallises out, leaving the remainder of the sodium chloride in solution.

The method usually adopted is to add the potassium chloride by degrees to the boiling solution of sodium nitrate, to remove the sodium chloride with a perforated ladle in proportion as it is deposited, and after allowing the liquid to rest for some time to deposit suspended impurities, to run it out into the crystallising pans.

The potassium-salt required for the conversion of sodium nitrate into potassium nitrate is sometimes obtained from the refuse of the beet-root employed in the manufacture of sugar.

Chili saltpetre sometimes contains a considerable proportion of iodate. Yellow samples containing chromate are occasionally found.

Potassium nitrate is sometimes prepared from the nitrates obtained in the *nitre-heaps*, which consist of accumulations of vegetable and animal refuse, with limestone, old mortar, ashes, &c. These heaps are constructed upon an impermeable clay floor under a shed to protect them from rain. One side of the heap is usually vertical and exposed to the prevailing wind, the other side being cut into steps or terraces. They are occasionally moistened with stable drainings, which are allowed to run into grooves cut in the steps at the back of the heap. In such a mass, at an atmospheric temperature between 60° and 70° F., nitrates of the various metals present in the heap are slowly formed, and, being dissolved by the moisture, are left by it, as it evaporates on the vertical side, in the form of an efflorescence. When this has accumulated in sufficient quantity, it is scraped off, together with a few inches of the *nitrified* earth, and extracted with water, which dissolves the nitrates, whilst the undissolved earth is built up again on the terraced back of the heap. After two or three years the heap is entirely broken up and reconstructed. The principal nitrates which are found dissolved in the water are those of potassium, calcium, magnesium, and ammonium, the three last of which may be converted into potassium nitrate by decomposing them with potassium carbonate.

The formation of nitrates in these heaps probably results from chemical changes similar to those which occur in the soils in which nitre is naturally formed, but, at present, these changes are not thoroughly explained. Some chemists are of opinion that nitrates are formed from atmospheric nitrogen and oxygen, encouraged by the presence of porous solids, and of matters undergoing oxidation. The explanation which is best supported by experimental evidence is that which refers their formation to the oxidation of ammonia (page 132), evolved by the putrefaction of the nitrogenised matters which the heaps contain, this oxidation also being much promoted by the presence of the strongly alkaline lime, of the porous materials capable of absorbing ammonia and presenting it under circumstances favourable to oxidation, and of a peculiar mycoderm or minute fungus (page 132).

In *refining saltpetre* for the manufacture of gunpowder, the impure (*grough*) salt is dissolved in about an equal weight of boiling water in a copper boiler, the solution run through cloth filters to remove insoluble matter, and allowed to crystallise in a shallow wooden trough lined with copper, the bottom of which is formed of two inclined planes (fig. 265). Whilst cooling, the solution is kept in continual agitation with wooden stirrers, in order that the saltpetre may be deposited in the minute crystals known as *saltpetre flour*, and not in the large prisms which are formed when the solution is allowed to crystallise tranquilly, and which contain within them cavities enclosing some of the impure liquor from which the saltpetre has been crystallised. The saltpetre, being so much less soluble in cold than in hot water, is, in great part, deposited as the liquid cools,

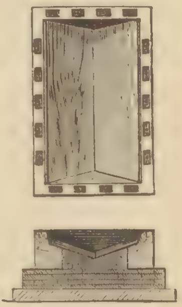
Fig. 265.

whilst the chlorides and other impurities, being present in small proportion, and not presenting the same disparity in their solubility at different temperatures, are retained in the liquid. The saltpetre flour is drained in a wooden trough with a perforated bottom, and transferred to a washing-cistern, where it is allowed to remain for half an hour in contact with two or three successive small quantities of water, to wash away the adhering impure liquor; it is then allowed to drain thoroughly, and in that state, containing from 3 to 6 per cent. of water, according to the season, is ready to be transferred to the incorporating mill or to a hot-air oven, where it is dried if not required for immediate use.

The mother-liquor, from which the saltpetre flour has been deposited, is boiled down and crystallised, the crystals being worked up with the next batch of grough nitre. The final washings of the flour are returned to the boiler in which the grough nitre is originally dissolved. When the saltpetre contains very much colouring matter, a little glue or animal charcoal is employed by the refiner to assist in its removal.

The impurities most objectionable in the saltpetre employed for gunpowder would be the chlorides of potassium and sodium, which cause it to absorb moisture easily from the air; the chief test, therefore, to which the refiner subjects it is the addition, to its solution in distilled water, of a few drops of solution of silver nitrate, which causes a milkiness, due to the separation of a precipitate of silver chloride, if the chlorides have not been entirely removed. Moreover, the sample should dissolve entirely in water, to a perfectly clear colourless solution, which should have no effect on blue or red litmus-paper, and should give no cloudiness with barium chloride (indicating the presence of sulphates), or with ammonium oxalate (indicating lime), when these are added to separate portions of it. Very minute quantities of sulphates and of lime, such as may have been derived from the use of river water in washing the flour, are generally disregarded.

Properties of saltpetre.—Potassium nitrate is usually distinguishable by the long striated or grooved six-sided prismatic form in which it crystallises (though it may also be obtained in rhombohedral crystals like those of sodium nitrate), and by the *deflagration* which it produces when thrown on red-hot coals. It fuses at about 635° F. (335° C.) to a colourless liquid, which solidifies on cooling to a translucent brittle crystalline mass. The *sal prunelle* of the shops consists of nitre which has been fused and cast into balls. At a red heat it effervesces from the escape of bubbles of oxygen, and is converted into potassium nitrite (KNO_2), which is itself decomposed by a higher temperature, evolving nitrogen and oxygen, and leaving a mixture of dipotassium oxide (K_2O) and potassium peroxide (K_2O_2). In contact with any combustible body, it undergoes decomposition with great rapidity, five-sixths of its oxygen being available for the oxidation of the combustible substance, and the nitrogen being evolved in the free state; thus, in contact with carbon, the complete decomposition of the nitre may be represented by the equation $2KNO_3 + C_8 = K_2CO_3 + CO_2 + CO + N_2$. Since the combustion of a large quantity of material may be thus effected in a very small space and in a short time, the temperature produced is much higher than that obtained by burning the combustible in the ordinary way. The specific gravity of saltpetre is 2.07, so that 1 cubic inch weighs

523 grains (obtained by multiplying the weight of a cubic inch of water, 252.5 grains, by 2.07). Since 202 grains (2 molecules) of nitre contain 80 grains (5 atoms) of oxygen available for the oxidation of combustible bodies, 523 grains (or 1 cubic inch of nitre) would contain 207 grains (or 605 cubic inches) of available oxygen, a volume which would be contained in about 3000 cubic inches of air; hence, 1 volume of saltpetre represents, in its power of supporting combustion, 3000 volumes of atmospheric air. It also enables some combustible substances to burn without actual flame, as is exemplified by its use in *touchpaper* or *slow port-fire*, which consists of paper soaked in a weak solution of saltpetre and dried, the combustion taking place between the *solid* combustible and the *solid* oxygen in the nitre, instead of between gases as in the case of flame.

If a continuous design be traced on foolscap paper with a brush dipped in a solution of 30 grains of saltpetre in 100 grains of water, and allowed to dry, it will be found that when one part of the pattern is touched with a red-hot iron, it will gradually burn its way out, the other portion of the paper remaining unaffected.

A mixture of 90 grains of saltpetre, 30 of sulphur, and 30 of moderately fine dried sawdust (*Baumé's flux*) will deflagrate with sufficient intensity to fuse a small silver coin into a globule; the mixture may be pressed down in a walnut shell or a small porcelain crucible, and the coin buried in it, the flame of a lamp being applied outside until deflagration commences.

Pulvis fulminans is a mixture of 3 parts of saltpetre, 1 part of sulphur, and 2 of potassium carbonate, all carefully dried; when it is heated on an iron plate, no action takes place till it melts, when it explodes very violently.*

CHARCOAL FOR GUNPOWDER.—Charcoal has been already described (p. 66) as the residue of the destructive distillation of wood, in which process the hydrogen and oxygen of the wood are for the most part expelled in the forms of wood naphtha (CH_4O), pyroligneous acid ($C_2H_4O_2$), carbonic acid gas, carbonic oxide, water, &c., leaving a residue containing a much larger proportion of carbon than the original wood, and therefore capable of producing a much higher temperature (page 71) by its combustion with the saltpetre. The higher the temperature to which the charcoal is exposed in its preparation, the larger the proportion of hydrogen and oxygen expelled, and the more nearly does the charcoal approach in composition to pure carbon; but it is not found advantageous in practice to employ so high a temperature, since it yields a dense charcoal of difficult combustibility, and therefore less fitted for the manufacture of powder. The average composition of wood, exclusive of ash, is, in 100 parts—50 parts carbon, 6 parts hydrogen, and 44 parts oxygen.

The composition of the charcoal prepared at different temperatures is given in the following table:—

Temperature of Charring.	Carbon.	Hydrogen.	Oxygen.	Ash.
270° C.	71.0	4.60	23.00	1.40
363°	80.1	3.71	14.55	1.64
476°	85.8	3.13	9.47	1.60
519°	86.2	3.11	9.11	1.58

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* Probably $2KNO_3 + K_2CO_3 + S_2 = K_2SO_4 + K_2S + CO_2 + NO + NO_2$. The NO and NO_2 would probably be decomposed into their elements by the violent detonation.

The charcoal employed for gunpowder in this country is prepared at temperatures between 360° C. and 520° C. It will be seen that the proportion of carbon, upon which the heating value of the charcoal depends, increases with the final temperature of carbonisation; but it has been found that the rapidity with which the temperature is raised has also a great effect in increasing the proportion of carbon, as shown in the following table:—

Final Temperature.	Time of Heating.	Percentage of Carbon.	Final Temperature.	Time of Heating.	Percentage of Carbon.
410° C.	5 hours	81.65	490° C.	2¾ hours	86.34
414°	2¾ ,,	83.14	555°	3¾ ,,	83.32
490°	3¼ ,,	84.19	558°	3 ,,	86.52

The charcoal prepared between 260° and 320° C. has a brown colour (*charbon roux*), and although it is more easily inflamed than the black charcoal obtained at higher temperatures, the presence of a large proportion of oxygen so much diminishes its calorific value, that its employment in gunpowder is not advantageous. It is used on the Continent in the manufacture of sporting-powder, and is prepared by exposing the wood, in an iron cylinder, to the action of high-pressure steam heated to about 280° C. Charcoal prepared at low temperatures gives somewhat higher velocities, but absorbs much more moisture than that prepared at high temperatures.

Light woods, such as alder, willow, and dogwood,* are selected for the preparation of charcoal for gunpowder, because they yield a lighter and more easily combustible charcoal, dogwood being employed for the best quality of powder for small arms. This wood is chiefly imported, since it has not been successfully grown in this country. The wood is stripped of its bark, and either exposed for a length of time to the air or dried in a hot chamber. Considerable loss of charcoal takes place if damp wood be charred, a portion of the carbon being oxidised by the steam at a high temperature.

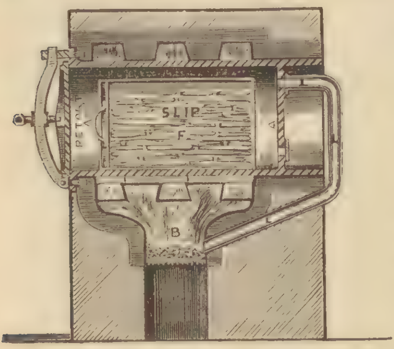

Fig. 266.—Charcoal retort.

In order to convert the wood into charcoal, 1½ cwt. of wood is packed into a sheet-iron cylinder or *slip* (fig. 266), one end of which is closed by a tightly fitting cover, and the other by a perforated plate, to allow of the escape of the gases and vapours expelled during the carbonisation. This cylinder is then introduced into a cylindrical cast-iron retort, built into a brick furnace, and provided with a pipe (L) for the escape of the products, which are usually carried back into the furnace (B) to be consumed. The process of charring occupies from 2½ to 3½ hours, and as soon as it is completed, which is known by the violet tint of the (carbonic oxide) flame from the pipe leading into the fire, the slip is transferred to an iron box or *extinguisher*, where the charcoal is allowed to cool. About 40 lbs. of charcoal are obtained from the above quantity of wood. Charcoal prepared by this process is spoken of as *cylinder charcoal*, to distinguish it from *pit charcoal*, prepared by the ordinary process of charcoal-burning described at page 67, and which is employed for fuze compositions, &c., but not for the best gunpowder. The fitness of the charcoal for the manufacture of powder is generally judged of by its physical characters. It is of course desirable that the charcoal should be as free from incombustible matter as possible. The proportion of the ash left by different charcoals varies considerably, but it seldom exceeds 2 per cent. This ash consists chiefly of the carbonates of potassium and calcium; it also contains calcium phosphate, magnesium carbonate, silicate and sulphate of potassium, chloride of sodium, and the oxides of iron and manganese.

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* Dogwood charcoal is not made from the true dogwood (*cornus*), but from the alder buckthorn (*Rhamnus frangula*), commonly called black dogwood.

The charcoal is kept for about a fortnight before being ground, for if ground when fresh, before it has absorbed moisture and oxygen from the air, it is liable to spontaneous combustion. The grinding is effected in a mill resembling a coffee-mill, and the charcoal is afterwards sifted.

The properties of charcoal have been already described; its great tendency to absorb moisture from the air is of some importance in the manufacture of gunpowder, from its causing a false estimate to be made of the proportion employed, unless the actual amount of water present in the charcoal is known.

Tar charcoal is the name given to sticks of charcoal which have accidentally become coated with a shining film of carbon left behind by tar which has condensed upon it in the retorts; it is sometimes rejected by the powder manufacturer.

The charcoal used in *cocoa-powder* appears to be made from rye-straw carbonised at a very low temperature so as to obtain a very brown charcoal poor in carbon (about 48 per cent. carbon and 4.75 per cent. hydrogen). In *Oliver powder*, part of the charcoal is replaced by uncarbonised peat.

SULPHUR FOR GUNPOWDER.—*Distilled sulphur* (page 187) is the variety always employed for the manufacture of gunpowder in the Government factory, the *sublimed sulphur* being employed for fuze compositions, &c. The alleged reason for the preference is that the sublimed sulphur, having been deposited in a chamber containing much sulphurous and sulphuric acid vapours,* its pores have become charged with acid which would be injurious in the powder; but it has been pointed out (page 189) that distilled sulphur consists entirely of the soluble or electro-negative variety of sulphur, whilst sublimed sulphur contains a large proportion of the insoluble or positive sulphur, which would probably influence its action in gunpowder. The sulphur should leave scarcely a trace of incombustible matter when burnt, and after stirring the powdered sulphur for some time with warm distilled water, the latter should only very feebly redden blue litmus. As an ingredient of gunpowder, sulphur is valuable on account of the low temperature (500° F.) at which it inflames, thus facilitating the ignition of the powder. Its oxidation by saltpetre is also attended with the production of a higher temperature than is obtained with charcoal, which has the effect of accelerating the combustion and of increasing, by expansion, the volume of gas evolved. The sulphur is ground under edge-runners (fig. 267) and sifted.

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* For certain compositions in which sublimed sulphur is used, it is well washed with water in order to remove the acid from its pores.

The difference in the inflammability of sulphur and charcoal is strikingly shown by heating a square of coarse wire-gauze over a flame till it is red hot in the centre, placing it over a jar of oxygen, allowing it to cool till it no longer kindles charcoal-powder sprinkled through it from a pepper-box, and whilst the cloud of charcoal is still floating in the gas, throwing in sulphur from a second box; the hot gauze will inflame the sulphur, and this will kindle the charcoal.

An iron rod allowed to cool below redness may be used to stir a mixture of charcoal with (3 parts of) nitre; but if dipped into powdered sulphur, at once inflames it, and the flame of the sulphur will kindle the mixture. The effect of the same rod upon mixtures of nitre with charcoal alone, and with charcoal and sulphur, is instructive.

The acceleration of the combustion of gunpowder by the sulphur is well shown by laying a train, of which one-half consists of a mixture of 75 nitre and 25 charcoal, and the other of 75 nitre, 15 charcoal, and 10 sulphur, a red-hot iron being applied at the junction of the two trains to start them together.

MANUFACTURE OF GUNPOWDER.—The proportions of the ingredients of gunpowder have been varied somewhat in different countries, the saltpetre ranging from 74 to 77 per cent., the charcoal from 12 to 16 per cent., and the sulphur from 9 to 12.5 per cent. English Government powder contains 75 per cent. of nitre, 15 per cent. of charcoal, and 10 per cent. of sulphur. An extra pound of saltpetre is generally added at Waltham, to compensate for loss in manufacture.

The powdered ingredients* are first roughly mixed in a revolving gun-metal drum, with mixing arms turning in an opposite direction, and the mixture is subjected, in quantities of about 50 lbs. at a time, to the action of the *incorporating mill* (fig. 267), where it is sprinkled with water, poured through the funnel (F), or from a can with a fine rose, and exposed to trituration and pressure under two cast-iron edge-runners (B), rolling round in different paths upon a cast-iron bed, a very intimate mixture being thus effected by the same kind of movement as in a common pestle and mortar, the distribution of the nitre through the mass being also assisted by its solubility in water. A wooden scraper (C) tipped with copper prevents the roller from getting clogged, and a *plough* (D) keeps the mixture in the path. Of course, the water employed to moisten the powder must be as free from deliquescent salts (especially chlorides, see page 442) as possible; at Waltham, condensed steam is employed: the quantity required varies with the state of the atmosphere. The duration of the incorporating process is varied according to the kind of powder required, the slow-

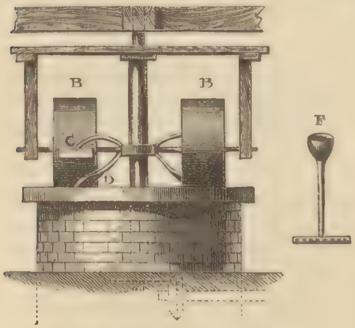

Fig. 267.—Incorporating mill.

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* The amount of water in the moist saltpetre (p. 442) is ascertained by drying and melting a weighed sample before the proportions are weighed out.

burning powder employed for cannon being sufficiently incorporated in about three hours, whilst rifle-powder requires five hours.

The dark grey mass of *mill-cake* which is thus produced contains 2 or 3 per cent. of water. It is broken up by passing between grooved rollers of gun-metal, and is then placed, in layers of about half an inch thick, between copper plates packed in a stout gun-metal box lined inside and outside with wood, in which it is subjected for a quarter of an hour to a pressure of about 70 tons on the square foot, in a hydraulic press, which has the effect of condensing a larger quantity of explosive material into a given volume, and of diminishing the tendency of the powder to absorb moisture from the air and to disintegrate or *dust* after granulation. The *press-cake* thus obtained is very hard and compact, resembling slate in appearance. As far as its chemical nature is concerned, it is finished gunpowder, but if it be reduced to powder and a gun loaded with it, the combustion of the charge is found to take place too slowly to produce its full effect, since the pulverulent form offers so great an obstacle to the passage of the flame by which the combustion is communicated from one end of the charge to the other. The press-cake must, therefore, be *granulated* (*corned*) or broken up into grains of sufficient size to allow the rapid passage of the flame between them, and the consequent rapid firing of the whole charge. The granulation is effected by crushing the press-cake between successive pairs of toothed gun-metal rollers, from which it falls on to sieves, which separate it into grains of different sizes, the dust, or *meal powder*, passing through the last sieve. At Waltham, the R.L.G. (rifle large grain) passes through a sieve of 4 meshes to the inch, and is retained on one of 8 meshes, whilst R.F.G. (rifle fine grain) passes through a 12-mesh, and is retained on a 20-mesh sieve. The granulated powders are freed from dust by passing them through revolving cylinders of wooden framework covered with canvas or wire cloth, and the fine-grain powder is glazed by the friction of its own grains against each other in revolving barrels. The large-grain powders are sometimes glazed or *faced* with graphite, by introducing a little of that substance into the glazing-barrels with the powder. The powder is dried in a chamber heated by steam, very gradually, so as not to injure the grain, and is once more dusted in canvas cylinders before being packed.

For very large charges, the grains having a diameter of $\frac{1}{4}$ to $\frac{1}{8}$ inch (R.L.G.) are found to burn too rapidly, exerting too great a strain upon the gun. In such cases, *pebble powder*, the grains of which vary from $\frac{5}{8}$ to $1\frac{1}{2}$ inch or more in diameter, is employed. *Prismatic powder* consists of large grains made of a regular six-sided prismatic form by compressing the powder-meal (without previously making it into press-cake) in moulds, with metal punches, whereas the pebble powder is irregular in form. The prismatic powder is made with perforations in the direction of its length to facilitate the passage of flame through the charge. *Pellet powder* is moulded in a similar manner into cylindrical pellets about $\frac{1}{2}$ inch long and $\frac{3}{4}$ inch in diameter, perforated at one end to about the centre.

Cocoa powder, or *brown powder*, is made with 79 per cent. nitre, 3 or 4 per cent. sulphur, and 15 per cent. of the brown charcoal from rye-straw (see p. 445). The small proportion of sulphur makes it burn slowly, notwithstanding the brown charcoal.

309. Properties of Gunpowder.—Good gunpowder is composed of hard angular grains, which do not soil the fingers, and have a perfectly uniform dark grey colour. Its specific gravity (*absolute density*), as determined by the *densimeter*,* varies between 1.67 and 1.84, and its *apparent density* (obtained by weighing a given measure of the grain against an equal measure of water) varies from 0.89 to 0.94, so that a cubic foot will weigh from 55 to 58 lbs. When exposed to air of average dryness, gunpowder absorbs from 0.5 to 1 per cent. of water. In damp air it absorbs a much larger proportion, and becomes deteriorated in consequence of the saltpetre being dissolved, and crystallising upon the surface of the grains. Actual contact with water dissolves the saltpetre and disintegrates the grains. When very gradually heated in air, gunpowder begins to lose sulphur, even at 212° F., this ingredient passing off rapidly as the temperature rises, so that the greater part of it may be expelled without inflaming the powder, especially if the powder is heated in carbonic acid gas or hydrogen, to prevent contact with air. If gunpowder be suddenly heated to 600° F. in air, it explodes, the sulphur probably inflaming first; but out of contact with air a higher temperature is required to inflame it. The ignition of gunpowder by flame is not ensured unless the flame be flashed among the grains of powder; it often takes some time to ignite powder with the flame of a piece of burning paper or stick, but contact with a red-hot solid body inflames it at once. A heap of good powder, when fired on a sheet of white paper, burns without sparks and without scorching or kindling the paper, which should exhibit only scanty black marks of charcoal after the explosion. If the powder has not been thoroughly incorporated, it will leave minute globules of fused nitre upon the paper. Two ounces of the powder should be capable of throwing a 68-lb. shot to a distance of 260 to 300 feet from an 8-inch mortar at 45° elevation.

This mode of testing powder by the *eprouvette* mortar is not now applied to Government powders. Far more accurate results are obtained by measuring the velocity imparted to a projectile of known weight by a given charge of the powder. The velocity is measured by means of a *chronoscope*, which registers the distance travelled by the shot in a given time by causing it to cut the wire of one electrical circuit at the commencement of its flight, and that of another at the conclusion, thus telegraphing its velocity to the instrument room at a distance.

Cannon powder (R.L.G.) is tested by firing a charge of 1 lb. from a muzzle-loader rifled gun, with a 12-lb. shot. Small-arm powder (R.F.G.) is fired from a Snider-Enfield or Martini-Henry rifle. The mean velocity at a distance of 105 feet from the muzzle is determined. For R.L.G. it amounts to about 1000 feet per second. A charge of 70 grs. of R.F.G. in the Snider-Enfield rifle gives a velocity somewhat greater than this.

Very fortunately, it is difficult to explode gunpowder by concussion, though it has been found possible to do so, especially on iron, and accidents appear to have been caused in this way by the iron edge-runners in the incorporating mill, when the workmen have neglected the special precautions which are laid down for them. The use of stone upon iron in the incorporation is avoided, because of the great risk of producing sparks, and copper is employed in the various fittings of a powder-mill wherever it is possible.

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* This is a simple apparatus for determining the weight of mercury displaced by a given weight of gunpowder, from which all the air has been exhausted.

The electric spark is, of course, capable of firing gunpowder, though it is not easy to ensure the inflammation of a charge by a spark unless its conducting power is slightly improved by mixing it with a little graphite, or by keeping it a little moist, which may be effected by introducing a minute quantity of calcium chloride.

310. PRODUCTS OF EXPLOSION OF GUNPOWDER.—In the explosion of gunpowder, the oxygen of the nitre converts the carbon of the charcoal chiefly into carbon dioxide (CO_2), part of which assumes the gaseous state, whilst the remainder is converted into potassium carbonate (K_2CO_3). The greater part of the sulphur is converted into potassium sulphate (K_2SO_4). The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur, and charcoal is resolved into a mixture of potassium carbonate, potassium sulphate, carbon dioxide, and nitrogen, the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effect of the explosion.

But in addition to these, several other substances are found among the products of the explosion. Thus, the presence of potassium sulphide (K_2S) may be recognised by the smell of hydric sulphide produced on moistening the solid residue in the barrel of a gun, and hydric sulphide (H_2S) itself may often be perceived in the gases produced by the explosion, the hydrogen being derived from the charcoal. A little marsh gas (CH_4) is also found among the gases, being produced by the decomposition of the charcoal, a portion of the hydrogen of which is also disengaged in the free state. Carbonic oxide (CO) is always detected among the products. It is evident that the collection for analysis of the products of explosion must be attended with some trouble, and that considerable differences are to be expected between the results obtained by different operators, from the variation of the circumstances under which the powder is fired and the products collected. When the powder is slowly fired, a considerable proportion of the nitrogen in the saltpetre is evolved in the form of nitric oxide gas (NO), which is not found among the products of the rapid explosion of powder.

Some of the most recent experiments upon the explosion of gunpowder have been made by Noble and Abel under conditions very similar to those which occur in practice, the powder having been confined in a strong vessel of mild steel, in which the powder was fired by electricity, so that the gaseous and solid products of the explosion remained within the vessel, and could be submitted to analysis. The great resources at the disposal of these experimenters render some account of their results instructive, though they add little to our knowledge of the principal reaction in the explosion of gunpowder, derived from the earlier experiments of Bunsen and Karolyi.

Three samples of powder manufactured at Waltham Abbey were thus examined. Their composition is stated in the following table:—

	Pebble Powder.	Rifle Large Grain.	Fine Grain.
Nitre	74.67	74.95	73.55
Sulphur	10.07	10.27	10.02
Charcoal, viz., Carbon	12.12	10.86	11.36
Hydrogen	0.42	0.42	0.49
Oxygen	1.45	1.99	2.57
Ash	0.23	0.25	0.17
Water	0.95	1.11	1.48
Potassium sulphate	0.09	0.15	0.36
	100.00	100.00	100.00

The quantities of gunpowder exploded in different experiments varied from 3½ oz. to 1 lb. 10 oz., and the pressures observed varied from 1 ton to over 36 tons on the square inch.

The solid products were found almost entirely collected at the bottom of the vessel, forming an exceedingly hard mass of a dark olive-green colour, exceedingly deliquescent, smelling strongly of hydric sulphide, and frequently also of ammonia. In some instances the solid residue was observed to become heated by exposure to air, from the rapid absorption of oxygen.

The following table shows the proportions of solid and gaseous products furnished by each powder, when the ratio between the volume of the charge and that of the containing space was varied so that the maximum pressures attained were those stated at the head of each column :—

	Pebble Powder.		Rifle Large Grain.		Fine Grain.	
Pressure, in tons per square inch	1.40	12.50	1.60	35.60	3.70	18.20
Weight of solid products from 100 parts powder	56.12	55.17	57.22	57.14	58.17	58.09
Weight of gaseous products from 100 parts powder	43.88	44.83	42.78	42.86	41.83	41.92

The permanent gases generated by the explosion were found to occupy, at 0° C. and at ordinary atmospheric pressure, about 280 times the volume of the original powder.

The products of explosion furnished by 1 gramme of each powder were—

	Pebble Powder.	Rifle Large Grain.	Fine Grain.
Potassium carbonate (K_2CO_3)	.3258	.3415	.2861
,, sulphate (K_2SO_4)	.0710	.0844	.1252
,, sulphide (K_2S)	.1042	.0807	.0999
,, sulphocyanide (KCNS)	.0014	.0013	.0007
,, nitrate (KNO_3)	.0013	.0015	.0009
Ammonium carbonate	.0005	.0004	.0003
Sulphur	.0445	.0490	.0381
Charcoal	.0008	.0004	...
Total solid products	.5495	.5592	.5512

	Pebble Powder.	Rifle Large Grain.	Fine Grain.
Carbonic acid gas (CO_2)	.2685	.2630	.2689
Carbonic oxide (CO)	.0477	.0422	.0355
Nitrogen	.1123	.1117	.1123
Sulphuretted hydrogen (H_2S)	.0111	.0109	.0101
Marsh gas (CH_4)	.0006	.0008	.0004
Hydrogen	.0006	.0009	.0007
Oxygen	...	.0002	.0003
Total gaseous products	.4408	.4297	.4282

From this table it appears that the solid residue of fired gunpowder consists chiefly of potassium carbonate and sulphate, with usually smaller proportions of potassium sulphide. The gases evolved are chiefly carbonic acid gas and nitrogen, with a small quantity of carbonic oxide.

The great variation in the proportions of sulphate and sulphide of potassium, coupled with our knowledge of the mutual relations of these bodies at high temperatures, would support the belief that the sulphate is first produced, and is partially converted into sulphide by secondary reactions.*

311. CALCULATION OF THE FORCE OF FIRED GUNPOWDER.—The complex character of the decomposition, and its variation under different conditions, render it impossible to write a single general equation representing the explosion of gunpowder; but in order to illustrate the method of calculating the force of fired powder in any given case, we may take the following equation as a simple expression of the principal reaction: $4KNO_3 + C_4 + S = K_2CO_3 + K_2SO_4 + N_4 + 2CO_2 + CO$.

The mechanical force exerted in explosion depends upon the production of a large volume of gas from a small volume of solid, the volume of the gas being increased by the expansive effect of the heat generated in the combustion of the charcoal and sulphur. To calculate the amount of this mechanical force, it is necessary to ascertain the volume of gas which would be evolved by a given volume of powder, and the extent to which the gas would be expanded by the heat at the instant of explosion.

It is calculated, from the Table of Atomic Weights, that—

$$\begin{array}{rcrcl}
4KNO_3 & = & 101 \times 4 & = & 404 \text{ grammes} \\
C_4 & = & 12 \times 4 & = & 48 \quad ,, \\
S & & & = & 32 \quad ,, \\
\hline
\text{Gunpowder} & & & . & 484 \quad ,,
\end{array}$$

$$\begin{array}{rcrcrcrcl}
 & & & & \text{Grammes.} & & \multicolumn{3}{l}{\text{Litres at } 0^\circ \text{ C. and } 760 \text{ mm. Bar.}} \\
N_4 & = & 14 \times 4 & = & 56 & = & 11.2 \times 4 & = & 44.8 \\
2CO_2 & = & 44 \times 2 & = & 88 & = & 22.4 \times 2 & = & 44.8 \\
CO & & & = & 28 & & & = & 22.4 \\
\hline
\multicolumn{3}{r}{\text{Gaseous products}} & & 172 \text{ grammes} & & & & 112.0 \text{ litres}
\end{array}$$

Hence it appears that 484 grammes of gunpowder would yield 112 litres of gas measured at 0° C. and 760 mm. barometric pressure.

We have next to determine the volume of this gas at the moment of the explosion.

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* The statement originally made by Noble and Abel, that potassium hyposulphite was an important constituent of the solid residue which had been overlooked by previous experimenters, was afterwards admitted to be due to a mistake in the analysis.

The total heat produced in the explosion of 1 part by weight of gunpowder was found by Noble and Abel to raise the temperature of 714.5 parts by weight of water from 0° C. to 1° C., or to raise the temperature of 1 part by weight of water from 0° C. to 714°.5 C., supposing the water to be capable of bearing so great an elevation of temperature without change of state or of specific heat.

This result is generally expressed by saying that the combustion of the powder evolves 714.5 *units of heat* (the unit of heat being the quantity required to raise 1 part by weight of water from 0° C. to 1° C.).

But the products of the explosion of powder will be raised to a higher temperature than 714°.5 C., because their specific heat is lower than that of water.

For the purpose of this calculation, the specific heat of a substance may be defined as the quantity of heat required to raise 1 gramme of the substance through 1° of the thermometer, water being taken as the unit.

It is evident that if the specific heat of each product of the explosion be multiplied by the actual weight of that product, the result will be the quantity of heat required to raise that product 1° in temperature.

The specific heats of the products have been ascertained by experiment, and are contained in the third column in the following table. The actual weight of each product from the explosion of 1 gramme of powder is contained in the second column, and the fourth column shows the quantity of heat required to raise each product 1° C. (representing as unity the quantity of heat required to raise 1 gramme of water from 0° C. to 1° C.).

Calculating from the above equation, the unit weight of gunpowder gives—

			Specific Heat.		
Potassium carbonate . . .	.28	×	.2162	=	.0605
,, sulphate	.36	×	.1901	=	.0684
Nitrogen	.12	×	.2438	=	.0293
Carbonic acid gas . . .	.18	×	.2163	=	.0389
,, oxide . . .	.06	×	.2450	=	.0147
					.2118

The quantity of heat, therefore, which is required to raise, through 1° C., the joint products of the explosion of 1 gramme of gunpowder is 0.2118 of the above-mentioned unit of heat.

Dividing the 714.5 units of heat generated in the explosion by the quantity of heat required to raise the joint products through 1°, we obtain 3373° C. for the number of degrees through which the products will be raised by the explosion.

The expansion of gases when heated amounts to $\frac{1}{273}$ of their volume at 0° for each degree of temperature.

Hence 3373° would expand the gas by $\frac{3373}{273}$ = (about) 12 times its volume at 0°, or each volume of gas at 0° would become 13 volumes at the moment of explosion.

The 112 litres of gas from 484 grammes of powder would become 112×13, or 1456 litres at the moment of explosion; and 1 gramme of powder would give $\frac{1456}{484}$, or 3.008 litres = 3008 cubic centimetres of gas.

In an ordinary charge of gunpowder, 1 gramme occupies a space of one cubic centimetre, but since, according to Noble and Abel, the fused solid products occupy one-third of the volume of the original powder charge, there would be ⅔ cubic centimetre to be occupied by the 3008 c.c. of gas.

Since the elastic force or pressure of gases increases in proportion as their volume is diminished, the 3008 c.c. of gas, when confined in a space which would contain only $\frac{2}{3}$ c.c. at the normal pressure of one atmosphere, must exert a pressure of $3008 \times \frac{3}{2} = 4512$ atmospheres or 4512×14.7 lbs., or 29.6 tons per square inch.

The experiments of Noble and Abel gave 280 volumes of gas at 0° from one volume of powder, instead of 231.4 volumes, as required by the equation; these 280 volumes would become 3640 volumes at the temperature of the explosion, and would exert a pressure of 5460 atmospheres in the space available for the gas; this amounts to nearly 36 tons per square inch.

Variations in the proportions of the ingredients of gunpowder have less effect upon the total energy of the powder than upon its rate of burning. Thus, a slowly burning powder containing a large proportion of charcoal will exert the same pressure in a closed vessel as is exerted by military powder. For, when the proportion of carbon is large, more of the oxygen of the nitre is converted into carbonic oxide and less into carbon dioxide; and a given quantity of oxygen, when converted into CO, gives twice as large a volume of gas as when converted into CO_2. But the formation of CO_2, from a given weight of oxygen, develops 1.6 times as much heat as that of CO, so that the thermal value of a powder varies inversely as the volume of gas measured at 0°; and the maximum pressure produced by the explosion is nearly the same for powders differing greatly in composition. This is illustrated by the results of Noble and Abel.

Powder.	Composition.			Thermal Value.	Gas at 0°.	Maxm. Pressure in Tons per Square Inch.
	Nitre.	Ch.	S.			
Mining . . .	67	19	14	509	360	44
Military . .	75	15	10	714	280	43

In calculating the pressure, it is supposed, of course, that the whole of the gas is evolved at once, and is immediately raised to the same temperature, conditions never fulfilled in the use of gunpowder in small arms or in cannon, where the combustion of the charge is not instantaneous, but rapidly progressive, where the confining space is rapidly enlarged by the movement of the projectile long before the whole of the charge has exploded, and where the heated gas is cooled by contact with the metal of the piece.

The calculation given above can be regarded only as an illustration of the method, as there are several circumstances which vitiate the conclusion arrived at. The chemical equation on which it is based is confessedly imperfect.

We know little or nothing of the real condition of the products at the moment of the explosion; it is probably very different from that after cooling, when we examine them. From what is known of the effect of heat upon carbonic acid gas and carbonic oxide, it is almost certain that these gases are at least partially resolved into their elements at the moment of explosion, and it is scarcely likely that the complex molecules of sulphate and carbonate of potassium would exist at so high a temperature. Any breaking up of the molecules of carbonic acid gas, of sulphate and carbonate of potassium, would increase the expansion, and render the above estimate of the force of fired powder too low.

If *dissociation* or temporary decomposition of the products occurs as a result of the high temperature, the acts of combination which must take place during the expansion and consequent cooling must be attended with evolution of heat, rendering the decrease of pressure more gradual than it would be otherwise.

The actual rate of expansion of gases at so high a temperature is inferred from our experience of their behaviour at comparatively low temperatures, and there are some indications of a want of agreement under the two conditions.

The experiments of Andrews have shown that, even at a pressure of 100 atmospheres, carbonic acid gas exhibits striking deviations from the law that the pressure exerted by a gas is inversely as its volume.

The period over which the combustion of a given weight of powder extends will, of course, depend upon the area of surface over which it can be kindled; thus a single fragment of powder weighing 10 grains, even if it were instantaneously kindled over its entire surface, could not evolve so much gas in a given time as if it had been broken into 10 separate grains, each of which was kindled at the same instant, since the inside of the large fragment can only be kindled from the outside. Upon this principle a given weight of powder in large grains will occupy a longer period in its explosion than the same weight in small grains, so that the large-grain powder is best fitted for ordnance, where the ball is very heavy, and the time occupied in moving it will permit the whole of the charge to be fired before the ball has left the muzzle, whilst in small arms with light projectiles, a finer grained and more quickly burning charge is required. If the fine-grain powder were used in cannon, the whole of the gas might be evolved before the containing space had been sensibly enlarged by the movement of the heavy projectile, and the gun would be subjected to an unnecessary strain; on the other hand, a large-grain powder in a musket would evolve its gas so slowly that the ball might be expelled with little velocity by the first half of it, and the remainder would be wasted. There is good reason to believe that even under the most favourable circumstances a large proportion of every charge of powder is discharged unexploded from the muzzle of the gun, and is therefore wasted. In blasting rocks and other mining operations, the space within which the powder is confined is absolutely incapable of enlargement until the gas evolved by the combustion has attained sufficient pressure to do the whole work, that is, to rend the rock, for example, asunder. Accordingly, a slowly burning charge will produce the effect, since the rock must give way when the gas attains a certain pressure, whether that happens in one second or in ten. Indeed, a slowly burning charge is advantageous, as being less liable to shatter the rock or coal, and bringing it away in larger masses with less danger. Barium nitrate and sodium nitrate are sometimes substituted for a part of the potassium nitrate in mining powder, its combustion being thus retarded.

The same charge of the same powder produces very different results when heated in different ways. If 5 grains of gunpowder be placed in a wide test-tube, and fired by passing a heated wire into the tube, a slight puff only is perceived; but if the same amount of powder be heated in the tube by a spirit-lamp, it will explode with a loud report, and perhaps shatter the tube (a copper or brass tube is safer). In the first place the combustion is propagated slowly from the particle first touched by the wire; in the second, all the particles are raised at once to pretty nearly the same temperature, and as soon as one explodes, all the rest follow instantaneously.

When gunpowder is slowly fired, the products of its decomposition are different from those mentioned above; thus, nitric oxide (NO), arising from incomplete decomposition of the nitre, is perceived in considerable quantity, and may be recognised by the red colour produced when it is brought in contact with air.

The white smoke resulting from the explosion of gunpowder consists chiefly of the sulphate and carbonate of potassium in a very finely divided state; it seems probable that at the instant of explosion they are converted into vapour, and are afterwards deposited in a state of minute division as the temperature falls. The *fouling* or actual solid residue in the gun is very trifling when the powder is dry and has been well incorporated; a damp or slowly burning powder leaves, as might be expected, a larger residue. The residue always becomes wet on exposure to air, from the great attraction for moisture possessed by the carbonate and sulphide of potassium.

When 10 grains of Waltham Abbey gunpowder are fired in a strong air-tight steel cylinder, with a cavity about an inch high and half an inch in diameter, by the galvanic battery, the interior of the cavity is covered with a snow-white powder composed of sulphate and carbonate of potassium, which deliquesces rapidly in a damp atmosphere. No nitric oxide is found in the gas formed by the explosion.

If a small quantity of powder be slightly damped and rammed into a wooden tube, in the mouth of which a piece of quick match is inserted, the charge may be kindled, and the tube held with its mouth under water, so that the gases may be collected in an inverted jar. These will be found to contain NO (giving a brown colour in contact with air), H_2S (giving a black precipitate with lead acetate), beside the CO_2 (giving a white precipitate with lime water), CO, and N.

The charge should be carefully rammed, and the wooden tube (or fuze) held with tongs, as it sometimes explodes.

312. *Effect of variations of atmospheric pressure on the combustion of gunpowder.*—From the circumstance that the combustion of gunpowder is independent of any supply of oxygen from the air, it might be supposed that it would be as easily inflamed *in vacuo* as under ordinary atmospheric pressure. This is not found to be the case, however, for a mechanical reason, viz., that the flame from the particles which are first ignited escapes so rapidly into the vacuous space, that it does not inflame the more remote particles. For a similar reason, charges of powder in fuzes are found to burn more slowly under diminished atmospheric pressure, the flame (or heated gas) escaping more rapidly and igniting less of the remaining charge in a given time. It has been determined that if a fuze be charged so as to burn for thirty seconds under ordinary atmospheric pressure (30 inches barometer), each diminution of 1 inch in barometric pressure will cause a delay of 1 second in the combustion of the charge, so that the fuze will burn for thirty-one seconds when the barometer stands at 29 inches.

The manufacture of gunpowder may be illustrated by the following experiments on a small scale:—

Preparation of the ingredients.—Charcoal.—A few small pieces of wood are placed in a clay crucible, which is then filled up with dry sand and heated in a moderate fire as long as any vapours are evolved, when it may be set aside to cool.

Sulphur.—500 grains of roll sulphur may be distilled in a Florence flask, using another flask, the neck of which has been cut off (fig. 268), for a receiver from which the sulphur is afterwards poured, in a melted state, upon a piece of tin-plate.

A plain retort with a wide short neck may be substituted for the Florence flask.

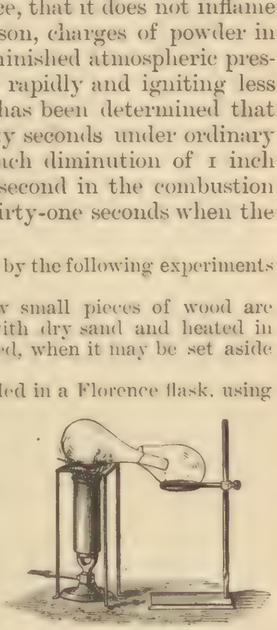

Fig. 268.—Distillation of sulphur.

Nitre.—1000 grains of impure nitre are dissolved, at a moderate heat, in 4 measured ounces of distilled water, in an evaporating dish (fig. 269); the solution is filtered into a beaker which is placed in cold water, and stirred with a glass rod until it is quite cold. The saltpetre flour thus obtained is collected upon a filter, thoroughly drained, the filter removed from the funnel, spread out, the saltpetre transferred to another piece of filter-paper, and pressed between the paper to remove as much of the liquid as possible; it is then spread out on paper and dried on a hot brick. (For the mode of testing its purity see page 442.)

Mixture of the ingredients.—Sixty grains of the charcoal, reduced to a very fine powder, 40 grains of the sulphur, also previously powdered, and 300 grains of the dried nitre, are very intimately mixed in a mortar; 50 grains of the mixture are set aside for comparison. To the remainder enough water is added to make it into a stiff cake, which is well incorporated under the pestle for some time. It is then scraped out of the mortar and allowed to dry slowly at a very gentle heat. When perfectly dry, it is crumbled to a coarse powder, and the dust sifted out through a piece of wire gauze. It will be found instructive to compare, in trains and otherwise, the firing of the powder in grains, of the dust, and of the mixed ingredients without incorporation, observing especially the difference in rapidity of burning and in the amount of residue.

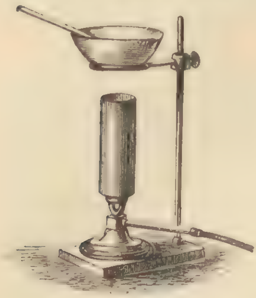

Fig. 269.

CHEMISTRY OF FUEL.

313. Several of the applications of chemical principles in the combustion of fuel have been already explained and illustrated. The object of this section is to compare the chemical composition of the most important varieties of fuel, and to exemplify the principles upon which their heating power may be calculated from the results furnished by their analysis.

All the varieties of ordinary fuel, of course, contain a large proportion of carbon, always accompanied by hydrogen, generally by oxygen, and sometimes by small proportions of nitrogen and sulphur. Certain mineral substances are also contained in all solid fuels, and compose the ash when the fuel is burnt.

For all practical purposes, it may be stated that the amount of heat generated by the combustion of a given weight of fuel depends upon the weights of carbon and hydrogen, respectively, which enter into combination with the oxygen *of the air* in the act of combustion of the fuel.

It has been ascertained by experiment that 1 lb. of carbon (in the form in which it exists in wood-charcoal), when combining with oxygen to form carbon dioxide, produces a quantity of heat which is capable of raising 8080 lbs. of water from 0° to 1° of the centigrade thermometer. This is usually expressed by saying that the *calorific value of carbon* is 8080, or that carbon produces 8080 *units of heat* during its combustion to carbon dioxide. If the fuel, therefore, consisted of pure carbon, it would merely be necessary to multiply its weight by 8080 to ascertain its calorific value.

One pound of hydrogen, during its conversion into water by combustion, evolves enough heat to raise 34,400 lbs. of water from 0° C. to 1° C., so that the *calorific value of hydrogen* is 34,400.

If the fuel consisted of carbon and hydrogen only, its calorific value would be calculated by multiplying the weight of the carbon in 1 lb. of the fuel by 8080, and that of the hydrogen by 34,400, when the sum of the products would represent the *theoretical* calorific value. But if the fuel contains oxygen already combined with it, the calorific value will be diminished, since less oxygen will be required from the air. For example, 1 lb. of wood contains 0.5 lb. of carbon, 0.06 of hydrogen, and 0.44 of oxygen. Now, oxygen combines with one-eighth of its weight of hydrogen to form water, so that the 0.44 lb. of oxygen will convert $.44 \div 8 = .055$ of the hydrogen into water, without evolution of available heat, leaving only 0.005 available for the production of heat. The calorific value of the wood, therefore, would be represented by the sum of 0.005×34400 $(=172)$ and 0.5×8080 $(=4040)$, which would amount to 4212; or 1 lb. of wood should raise 4212 lbs. of water from 0° C. to 1° C.

These considerations lead to the following *general formula for calculating the calorific value of a fuel* containing carbon, hydrogen, and oxygen, where c, h, and o, respectively represent the carbon, hydrogen, and oxygen in 1 grain of fuel.

The calorific value (or number of lbs. of water which might be heated by the fuel from 0° C. to 1° C.) $= 8080\,c + 34400\left(h - \frac{o}{8}\right)$ or $8080\,c + 34000\,h - 4300\,o$.

The calorific value of a fuel, as determined by experiment, is generally less than would be calculated from its chemical composition, in consequence of the absorption of a certain amount of heat attending the chemical decomposition of the fuel. In the case of compounds of carbon and hydrogen, it has been observed that even when they have the same composition in 100 parts, they have not of necessity the same calorific value, the latter being affected by the difference in the arrangement of the component particles of the compound, which causes a difference in the quantity of heat absorbed during its decomposition. Thus, olefiant gas (C_2H_4) and cetylene ($C_{16}H_{32}$) have the same percentage composition, and their calculated calorific values would be identical, but the former is found to produce 11,858 units of heat, and the latter only 11,055. As a general rule, however, it is found that the calorific values of the hydrocarbons which contain a multiple of CH_2, agree more nearly with the calculated numbers than do those of hydrocarbons which belong to the marsh-gas series.

It must be remembered that the calorific value of a fuel represents the actual amount of heat which a given weight of it is capable of producing, and is quite independent of the manner in which the fuel is burnt. Thus, a hundredweight of coal will produce precisely the same amount of heat in an ordinary grate as in a wind-furnace, though in the former case the fire will scarcely be capable of melting copper, and in the latter it will melt steel. The difference resides in the *temperature* or *calorific intensity* of the two fires: in the wind-furnace, through which a rapid draught of air is maintained by a chimney, a much greater weight of atmospheric oxygen is brought into contact with the fuel in a given time, so that, *in that time*, a greater weight of fuel will be consumed and more heat will be produced; hence the fire will have a higher temperature, for the temperature represents, not the quantity of heat present in a given mass of matter, but the intensity or extent to which that heat is accumulated at any particular point. In the case of the wind-furnace here cited, a further advantage is gained from the circumstance that the rapid draught of air allows a given weight of fuel to be consumed in a smaller space, and, of course, the smaller the area over which a given quantity of heat is distributed, the higher is the temperature within that area (as exemplified in the use of the common burning-glass). In some of the practical applications of fuel, such as heating steam-boilers and warming buildings, it is the *calorific value* of the fuel which chiefly concerns us; but the case is different where metals are to be melted, or chemical changes to be brought about by the application of a very high temperature, for it is then the *calorific intensity*, or actual temperature of the burning mass, which has to be considered. No accurate method has yet been devised for determining by direct experiment the calorific intensity of fuel, and it is therefore ascertained by calculation from the calorific value.

Let it be required to calculate the calorific intensity, or actual temperature, of carbon burning in pure oxygen gas.

Twelve lbs. of carbon combine with 32 lbs. of oxygen, producing 44 lbs. of CO_2; hence 1 lb. of carbon combines with 2.67 lbs. of oxygen, producing 3.67 lbs. of CO_2. It has been seen above that 1 lb. of carbon evolves 8080 units of heat, or is capable of raising 8080 lbs. of water from 0° to 1° C., or, on the supposition that the water would bear such an elevation of temperature, and that its specific heat would remain constant, the 1 lb. of carbon would raise 1 lb. of water from 0° to 8080° C. If the *specific heat* (or heat required to raise 1 lb. through 1°—see page 452) of CO_2 were the same as that of water, 8080° divided by 3.67 would represent the temperature to which the 3.67 lbs. of CO_2 would be raised, and therefore the temperature to which the solid carbon producing it would be raised in the act of combustion. But the specific heat of carbonic acid gas is only 0.2163, so that a given amount of heat would raise 1 lb. of CO_2 to nearly five times as high a temperature as that to which it would raise 1 lb. of water.

Dividing the 8080 units of heat (available for raising the temperature of the CO_2) by 0.2163 (the quantity of heat required to raise 1 lb. of CO_2 through 1°), we obtain 37355 for the number of degrees through which 1 lb. of CO_2 might be raised by the combustion of 1 lb. of carbon. But there are 3.67 lbs. of CO_2 formed in the combustion, so that the above number of degrees must be divided by 3.67 in order to obtain the actual temperature of the CO_2 at the instant of its production, that is, the temperature of the burning mass. The calorific intensity of carbon burning in pure oxygen is therefore (37355° C. ÷ 3.67 =) 10178° C. (or 18352° F.). But if the carbon be burnt in air, the temperature will be far lower, because the nitrogen of the air will absorb a part of the heat, to which it contributes nothing. The 2.67 lbs. of oxygen required to burn 1 lb. of carbon would be mixed, in air, with 8.93 lbs. of nitrogen, so that the 8080 units of heat would be distributed over 3.67 lbs. of carbonic acid gas and 8.93 lbs. of nitrogen. Since the specific heat of carbonic acid gas is 0.2163, the product of 3.67×0.2163 (or 0.794) represents the quantity of heat required to raise the 3.67 lbs. of CO_2 from 0° to 1° C.

The specific heat of nitrogen is 0.2438; hence 8.93×0.2438 (or 2.177) represents the quantity of heat required to raise the 8.93 lbs. of atmospheric nitrogen from 0° to 1° C.

Adding together these products, we find that $0.794 + 2.177 = 2.971$ represents the quantity of heat required to raise both the nitrogen and carbonic acid gas from 0° to 1° C.

Dividing the 8080° by 2.971, we obtain 2720° C. (4928° F.) for the number of degrees through which these gases would be raised in the combustion, *i.e.*, for the calorific intensity of carbon burning in air. By heating the air before it enters the furnace (as in the hot-blast iron furnace), of course the calorific intensity would be increased; thus, if the air be introduced into the furnace at a temperature of 600° F., it might be stated, without serious error, that the temperature producible in the furnace would be 5528° F. (4928° + 600°.). The temperature might be further increased by diminishing the area of combustion, as by employing very compact fuel and increasing the pressure of the blast.

In calculating the calorific intensity of hydrogen burning in air, from its calorific value, it must be remembered that, in the experimental determination of the latter number, the steam produced in the combustion was condensed to the liquid form, so that its latent heat was added to the number representing the calorific value of the hydrogen; but the latent heat of the steam must be *deducted* in calculating the calorific intensity, because the steam goes off from the burning mass and carries its latent heat with it.

One lb. of hydrogen, burning in air, combines with 8 lbs. of oxygen, producing 9 lbs. of steam, leaving 26.77 lbs. of atmospheric nitrogen, and evolving 34400 units of heat.

It has been experimentally determined that the latent heat of steam is 537° C., that is, 1 lb. of water, in becoming steam, absorbs 537 units of heat (or as much heat as would raise 537 lbs. of water from 0° to 1° C.) without rising in temperature as indicated by the thermometer. The 9 lbs. of water produced by the combustion of 1 lb. of hydrogen will absorb, or render latent, 537 × 9 = 4833 units of heat. Deducting this quantity from the 34400 units evolved in the combustion of 1 lb. of hydrogen, there remain 29567 units of heat available for raising the temperature of the 9 lbs. of steam and 26.77 lbs. of atmospheric nitrogen. The specific heat of steam being 0.480, the number (0.480 × 9 =) 4.32 represents the quantity of heat required to raise the 9 lbs. of steam through 1° C.; and the specific heat of nitrogen (0.2438) multiplied by its weight (26.77 lbs.) give 6.53 units of heat required to raise the 26.77 lbs. of nitrogen through 1° C. By dividing the available heat (29567 units) by the joint quantities required to raise the steam and nitrogen through 1° C. (4.32 + 6.53 = 10.85), we obtain the number 2725° C. (4937° F.) for the calorific intensity of hydrogen burning in air.

The method of calculating the calorific intensity of a fuel composed of carbon, hydrogen, and oxygen will now be easily followed.

Let c and h respectively represent the weights of carbon and hydrogen in 1 lb. of fuel, and o that of oxygen. Then $\frac{o}{8}$ = weight of hydrogen required to convert the oxygen into water, and $h - \frac{o}{8}$ represents the hydrogen which is available for the production of heat. $8080\,c + 34400\left(h - \frac{o}{8}\right)$ represents the calorific value in ° C., $= 8080\,c + 34400\,h - 4300\,o$.

$2.67\,c$ = atmospheric oxygen consumed by the carbon; $8\left(h - \frac{o}{8}\right)$ or $8\,h - o$ = atmospheric oxygen consumed by the hydrogen available as fuel.

$3.34\,(2.67\,c + 8\,h - o)$ = atmospheric nitrogen $= 8.92\,c + 26.72\,h - 3.34\,o$.

Multiplying this by the specific heat of nitrogen 0.2438, we obtain—

$2.17\,c + 6.51\,h - 0.81\,o$ for the heat required to raise the nitrogen through 1° C.

$0.794\,c$ represents the quantity of heat required to raise the CO_2 through 1° C., and $4.32\,h$ is the heat required to raise the steam through 1°. Accordingly, the available heat, $8080\,c + 34400\,h - 4300\,o$, must be divided by $0.794\,c + 4.32\,h + (2.17\,c + 6.51\,h - 0.81\,o)$, or $2.96\,c + 10.83\,h - 0.81\,o$ in order to obtain the calorific intensity.

Hence, the calorific intensity, in centigrade degrees, of a fuel composed of carbon, hydrogen, and oxygen, is represented by the formula—

$$\frac{8080\,c + 34400\,h - 4300\,o}{2.96\,c + 10.83\,h - 0.81\,o}$$

The actual calorific intensity of the fuel is not so high as it should be according to theory, because a part of the carbon and hydrogen is converted into gas by destructive distillation of the fuel, and this gas is not actually burnt *in the fire*, so that its calorific intensity is not added to that of the burning solid mass. Again, a portion of the carbon is converted into carbonic oxide (CO), especially if the supply of air be imperfect, and much less heat is produced than if the carbon were converted into carbon dioxide; although it is true that this carbonic oxide may be consumed above the fire by supplying air to it, the heat thus produced does not increase the calorific intensity of temperature of the fire itself.

One lb. of carbon furnishes 2.33 lbs. of carbonic oxide. These 2.33 lbs. of carbonic oxide evolve, in their combustion, 5599 units of heat. But if the 1 lb. of carbon had been converted at once into carbon dioxide, it would have evolved 8080 units of heat, so that 8080 – 5599, or 2481. represents the heat evolved during the conversion of 1 lb. of carbon into carbonic oxide, showing that a considerable loss of heat *in the fire* is caused by an imperfect supply of air. It has been already pointed out, in the section relating to Coal, that the formation of carbonic oxide is sometimes encouraged with a view to the production of a flame from non-flaming coal, such as anthracite.

The actual calorific intensity of fuel is diminished by the heat consumed in bringing the portion of fuel yet unconsumed, as well as the surrounding parts of the grate, up to the temperature of the fire.

The following table exhibits the average percentage composition of the principal varieties of fuel (exclusive of ash), together with their calculated calorific values and intensities:—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Calorific	
						Value.	Intensity.
Wood (Oak) . .	50.18	6.08	43.74	...	...	4212° C.	2380° C.
Peat . . .	61.53	5.64	32.82	...	...	5654	2547
Lignite (Bovey) .	67.86	5.75	23.39	0.57	2.41	6569	2628
Bituminous coal .	79.38	5.34	13.01	1.85	0.39	7544	2694
Charcoal . .	90.44	2.91	6.63	...	...	8003	2760
Anthracite . .	91.86	3.33	3.02	0.84	0.92	8337	2779
Coke . . .	97.34	0.49	0.97		1.20	8009	2761
Petroleum . .	85.00	13.00	2.00	...	...	14011*	...

In all ordinary fires and furnaces, a large amount of heat is wasted in the current of heated products of combustion escaping from the chimney. Of course, a portion of this heat is necessary in order to produce the draught of the chimney. In boiler furnaces it is found that, for this purpose, the temperature of the air escaping from the chimney must not be lower than from 500° to 600° F. If the fuel could be consumed by supplying only so much air as contains the requisite quantity of oxygen, a great saving might be effected, but in practice about twice the calculated quantity of air must be supplied in order to effect the removal of the products of combustion with sufficient rapidity.

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* Calculated for gaseous carbon (see p. 461).

Much economy of fuel results from the use of furnaces constructed on the principle of Siemens' *regenerative furnace*, in which the waste heat of the products of combustion is absorbed by a quantity of firebricks, and employed to heat the air before it enters the furnace, two chambers of firebricks doing duty alternately, for absorbing the heat from the issuing gas, and for imparting heat to the entering air, the current being reversed by a valve as soon as the firebricks are strongly heated.

It was shown, at page 89, that the true calorific value of carbon *in the state of gas* is 11214, instead of 8080, as in the case of solid carbon. Hence, in calculating the calorific value and intensity of gaseous or vaporous fuel containing carbon, the number 11214 must be substituted for 8080. Moreover, in burning gas or vapour, heat is not so freely imparted to the solid material of the furnace, so that recent advances in the economy of fuel for producing high temperatures have been in the direction of employing gaseous fuel, such as that from Siemens' *producers*, or vapours, such as that of petroleum.

A very useful formula for calculating the value of coal is that of Cornut; $Q = 8080C' + 11214C'' + 34462H$, where Q = quantity of heat, C' = carbon left as coke on distilling the coal, and C'' = carbon contained in the volatile products.

If much oxygen is present, one-eighth of its weight must be deducted from the hydrogen.

(For the principles of smoke prevention, and other particulars of the chemistry of fuel, see *Coal*.)

ORGANIC CHEMISTRY.

314. The division of chemistry into inorganic and organic was originally intended to distinguish mineral substances from those derived from animal and vegetable life; but since many of the latter may now be produced in the laboratory from the elements obtainable from mineral sources, it has become usual to define organic chemistry as the chemistry of the compounds of carbon, since this element is always present in the substances formerly spoken of as organic.

Organic chemistry differs from inorganic in being chiefly concerned with the compounds produced by the arrangement, in different proportions or in different positions, of the elements carbon, hydrogen, oxygen, and nitrogen, though the other elements occasionally enter into the composition of organic compounds.

A useful practical distinction between organic and inorganic substances is afforded by their behaviour when heated. An organic substance is either converted into vapour when moderately heated, or is decomposed into volatile products, generally leaving a residue of charcoal, which burns away when heated in air.

Upon this is based the *ultimate analysis of organic compounds* for the purpose of ascertaining the relative proportions of their elements.

The *making a combustion*, as it is technically called, consists in burning the organic compound so as to convert its carbon into CO_2 and its hydrogen into H_2O, from the weight of which the proportions of those elements are obtained by calculation. The substance to be analysed, having been carefully dried and weighed (about 0.5 grm.), is placed in a small boat-shaped tray of porcelain or platinum, which is introduced into one end of a glass tube about 30 inches long, of which about 24 inches are filled with small fragments of carefully dried cupric oxide. The end of the tube where the boat is placed is connected with an apparatus for transmitting air or oxygen, which has been purified from CO_2 by passing through potash, and from H_2O by calcium chloride. To the other end of the tube is attached, by a perforated cork, a weighed tube (B) filled with small fragments of calcium chloride to absorb H_2O, and to this is joined, by a caoutchouc tube, a *bulb-apparatus* (C) containing strong potash to absorb CO_2, and a small *guard-tube* with calcium chloride to prevent loss of water from the potash. The *potash-bulbs*

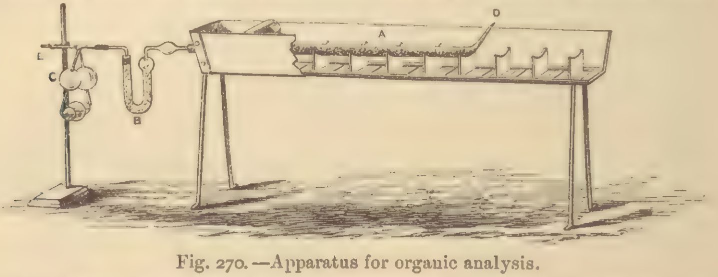

Fig. 270.—Apparatus for organic analysis.

and guard-tube are accurately weighed. The *combustion-tube* is supported in a charcoal- or gas-furnace, and that portion which contains the cupric oxide is heated to redness. The end containing the boat is then gradually heated, so that the organic substance is slowly vaporised or decomposed. The vapour or the products of decomposition, in passing over the red-hot cupric oxide, will acquire the oxygen necessary to convert the C into CO_2 and the H into H_2O, which are absorbed in the potash-bulbs and calcium-chloride tube. At the end of the process, which commonly occupies about an hour, a slow stream of pure air or oxygen is passed through, whilst the entire tube is red hot, in order to burn any charcoal which may remain in the boat, and to carry forward all the CO_2 and H_2O into the absorption apparatus. The weight of the CO_2 is given by the increase in weight of the potash-bulbs, and that of H_2O by that of the calcium chloride.

In some cases, it is preferable to mix the substance with a large quantity of powdered cupric oxide, so that the mixture may occupy about twelve inches of an eighteen-inch tube (fig. 270), with a layer of three inches of cupric oxide before and behind it. The hinder end of the tube is then often drawn out and sealed, as at D, the point being broken off when the combustion is finished, and a slow stream of air drawn through by gentle suction at the opening (E) of the potash-bulbs. In the case of substances difficult of combustion, the cupric oxide is replaced by lead chromate, $PbCrO_4$, which evolves oxygen when heated.

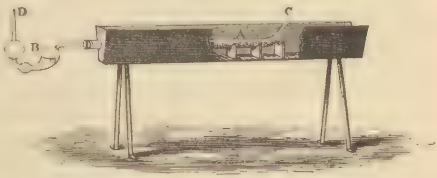

Fig. 271.—Estimation of nitrogen.

When nitrogen is present in the substance, it may be partly converted into N_2O_3 or NO_2, which would increase the weight of the absorption-apparatus. To avoid this, three or four inches of the front end of the combustion-tube are filled with metallic copper, which, being heated to redness, absorbs the O from the N_2O_3 or NO_2, leaving N, which passes through the absorption-apparatus and escapes. When it is desired to make a *determination of the nitrogen*, the combustion-tube is arranged in the same way, but the absorption-apparatus is replaced by a bent tube to permit the collection of the gas in a measured tube filled with strong potash. Before commencing the combustion, the air is swept out of the tube by a stream of pure CO_2, which is continued during the combustion, and is absorbed by the potash, the nitrogen being collected and measured.

Another method of estimating nitrogen in organic substances consists in heating them with a mixture of hydrates of sodium and calcium (*soda-lime*), when the N is evolved as NH_3, which is absorbed by hydrochloric acid, and precipitated by platinic chloride, the weight of N being calculated from that of the $PtCl_4.2NH_4Cl$ obtained.

Sulphur and *phosphorus* are estimated in organic compounds by converting them into sulphuric and phosphoric acids by the action of powerful oxidising agents (nitric acid, chloric acid, bromine, &c.), and determining these acids by the usual methods.

The proportion of *oxygen* in an organic substance is generally ascertained by difference, that is, by deducting the sum of the weights of all the other elements from the total weight of the substance.

As an example of the ultimate analysis of an organic compound, that of alcohol may be given (volatile liquids are weighed in a small glass bulb with a thin stem, the end of which is sealed for weighing, and broken off when the bulb is introduced into the combustion-tube):—

.5 grm. alcohol, burnt with cupric oxide, as above, gave .9565 grm. CO_2 and .5869 grm. H_2O.

Since 44 grms. CO_2 contain 12 grms. C., $\frac{12}{44}$ of .9565, or .2608, is the weight of C found.

Since 18 grms. H_2O contain 2 grms. H, $\frac{2}{18}$ of .5869, or .0652, is the weight of H found.

The sum of the C and H is .2608 + .0652, or .3260. Deducting this from .5 grm. alcohol, we have .174 grm. for the weight of O contained in it.

So that .5 grm. alcohol contains—

.2608	grm.	carbon	or	52.16	per cent.
.0652	,,	hydrogen	,,	13.04	,,
.1740	,,	oxygen	,,	34.80	,,

It is usual to express the results of such an analysis in an *empirical formula*, which gives, in the simplest form, the relative numbers of atoms of the elements present.

315. *To deduce the empirical formula from the percentage composition*, we divide the percentage of each element by its atomic weight, and express the ratio of the resulting quotients in its lowest terms; thus—

52.16	divided by	12 gives	4.34	atomic weights of	carbon
13.04	,,	1 ,,	13.04	,, ,,	hydrogen
34.80	,,	16 ,,	2.17	,, ,,	oxygen

If the ratio 4.34 : 13.04 : 2.17 be expressed in its lowest terms, it becomes 2 : 6 : 1, giving for the *empirical formula* of alcohol, C_2H_6O.

The question now arises whether this formula is a true representation of the molecule or indivisible particle of alcohol, or whether the molecule should be written $C_4H_{12}O_2$, or $C_6H_{18}O_3$, or in any other form which would preserve the ratio established beyond dispute by the above analysis.

316. *To deduce the molecular formula of a compound from its empirical formula* we must determine the molecular weight of the compound, for it is evident that the formula C_2H_6O represents 2 atoms of C, weighing 12 × 2, 6 atoms of H, weighing 1 × 6, and 1 atom of O, weighing 16; the sum of these numbers, or 46, would be the weight of alcohol represented by C_2H_6O, whereas the formula $C_4H_{12}O_2$ would express 46 × 2 parts by weight, and $C_6H_{18}O_3$ would express 46 × 3 parts by weight of alcohol.

The molecular weight of a compound is that weight which, when converted into vapour, occupies the same volume as two parts by weight of hydrogen at the same temperature and pressure (see p. 3). Hence, one method of *determining the molecular weight of a compound* is to convert a definite weight of it into vapour, and to compare the volume of the vapour with that which an equal weight of hydrogen would occupy at the same temperature and pressure.

The operation is termed the *determination of vapour-density*. The easiest method of effecting it is that of Victor Meyer, in which a weighed quantity of the substance is converted into vapour in a vessel containing air, and the volume of air displaced by the vapour is collected and measured.

Take, for example, the determination of the vapour-density of alcohol.

The vaporising-tube (*b*, fig. 272), well closed by a cork, is heated in the cylinder of boiling water (*a*) as long as any bubbles of air pass from the opening of the delivery-tube (*d*) through the water in the trough. The end of the delivery-tube is then inserted into the measured tube (*f*), which is full of water. About 0.1 grm. of alcohol is weighed out in a small tube, which is dropped into the opening of the vaporising-tube, this being then quickly corked. A little asbestos is placed at the bottom of the vaporising-tube (*c*) to prevent breakage.

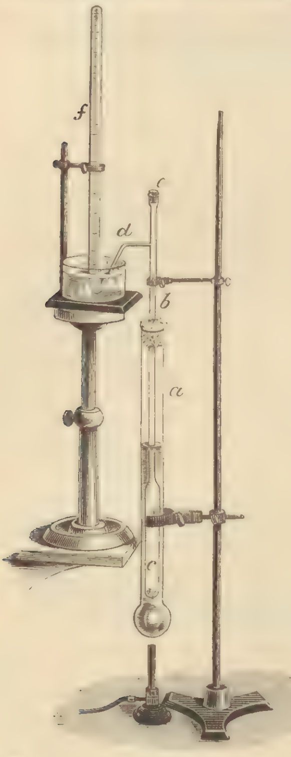

Fig. 272.—Victor Meyer's apparatus.

The alcohol-vapour expels a volume of air equal to its own, which is collected in the tube (*f*) and accurately measured, with the usual corrections for temperature and pressure. The volume of a known weight of alcohol in the form of vapour having been thus ascertained, the vapour-density may be calculated. For example, 0.1 grm. of alcohol expelled 48.5 c.c. of air corrected to 0° and 760 mm. Bar. Hence, supposing that alcohol could retain the state of vapour at that temperature and pressure, 48.5 c.c. of alcohol vapour would weigh 0.1 grm. Now, 0.1 grm. of hydrogen measures 1116 c.c. at 0° and 760 mm. So that the vapour-density of alcohol, referred to hydrogen as the standard, is $\frac{1116}{48.5} = 23$, or 23 parts by weight of alcohol vapour occupy the same volume as 1 part of hydrogen, so that the molecular weight of alcohol is 23 × 2, or 46.

The alcohol was found to contain (p. 464), in 100 parts, 52.16 C, 13.04 H, and 34.8 O; the weight of each element contained in the molecule, or 46 parts by weight, of alcohol will be found by the proportions—

100 : 46 :: 52.16 : 23.994 C in a molecule of alcohol
" " 13.04 : 5.998 H " "
" " 34.8 : 16.008 O " "

These numbers are sufficiently near to 24 or two atoms of C, 6 atoms of H, and 16, or one atom of O, showing that the molecular formula of alcohol is C_2H_6O.

In the case of a substance which cannot be converted into vapour without decomposition, the molecular weight is inferred from a consideration of the chemical relations of the substance, and its determination is sometimes a difficult matter. The general character of the method will be seen from the following example, selected on account of its simplicity, though referring to a substance which may be vapourised without decomposition.

Determination of the molecular formula of an acid.—The substance yielded, on combustion with cupric oxide, in 100 parts—carbon 40, hydrogen 6.66, oxygen 53.33; which lead to CH_2O as the simplest formula, or empirical formula of the acid.

By neutralising the acid with ammonia, and stirring with solution of silver nitrate, a crystalline silver salt was obtained, which was purified by recrystallisation from hot water, dried, weighed in a porcelain crucible of known weight, and gradually heated to redness. On again weighing the crucible after cooling, it was found to contain a quantity of metallic silver amounting to 64.66 per cent. of the weight of the salt. Now, as a general rule, a silver-salt is formed from an acid by the displacement of an atom of hydrogen by an atom of silver; so that what remains of a silver salt, after deducting the silver, represents the acid itself *minus* a quantity of hydrogen equivalent to the silver.

From the silver salt	100.00
Deduct the silver	64.66
Acid residue	35.34

$$\text{Then } 64.66\ \text{Ag} : 108 \left\{\begin{matrix}\textit{Ag in one mole-}\\ \textit{cule of the salt}\end{matrix}\right\} :: 35.34 : 59 \left\{\begin{matrix}\textit{acid residue in}\\ \textit{one molecule}\end{matrix}\right.$$

To the acid residue	59
Add the hydrogen equivalent to an atom of Ag	1
Molecular weight of the acid . .	60

The formula CH_2O represents $12 + 2 + 16 = 30$. Hence the molecular formula is $C_2H_4O_2 = 60$; and the silver-salt is $C_2H_3AgO_2$, which is the formula of silver acetate. Hence the acid analysed was acetic acid.

Determination of the molecular formula of an organic base.—The substance yielded, on combustion with cupric oxide, in 100 parts, carbon 77.42, hydrogen 7.53. A determination of nitrogen gave 15.05 per cent., so that there was no oxygen. These numbers lead to C_6H_7N as the simplest or empirical formula of the base. By dissolving the base in hydrochloric acid and adding platinic chloride, a yellow crystalline precipitate was obtained, resembling the ammonio-platinic chloride formed when ammonia is treated in the same way. This precipitate was washed with alcohol, dried, weighed in a porcelain crucible, and heated to redness, when it left a residue of metallic platinum, which amounted to 32.98 per cent. of the weight of the salt. As a general rule, a platinum-chloride salt is formed by the combination of $PtCl_4$ with two molecules of the hydrochloride of the base; in the case of the ammonio-platinic chloride, the formula is $PtCl_4.2(NH_3.HCl)$; so that what remains of a platinum salt after deducting the platinum represents two molecules of the base + two molecules of HCl + 4 atoms of chlorine.

From the platinum salt 100.00
Deduct the platinum . . . 32.98

Remainder 67.02

$$\text{Then } 67.02 \text{ Pt} : 197 \left\{\begin{matrix}\text{Pt in one mole-}\\ \text{cule of the salt}\end{matrix}\right\} :: 32.98 : 400.3$$

Hence 2 mols. base + 2 mols. HCl + 4 atoms Cl = 400.3
Deduct $2HCl + Cl_4$ = 215.0

Weight of two molecules of the base . 185.3

The molecular weight of the base, therefore, is 92.6. The formula C_6H_7N represents $72 + 7 + 14 = 93$. This is therefore the molecular formula, and the base is *aniline.*

The *law of even numbers* is sometimes a useful guide in fixing molecular formulæ. Since carbon generally behaves as a tetrad element (see p. 7), the *atom-fixing power of any group of carbon atoms must be represented by an even number.* Thus, a single carbon atom would be C^{iv}, indicating its power of attaching to itself 4 hydrogen atoms. A *chain* of two carbon atoms would be C^{vi}_2, if the two atoms were *singly-linked* or united by one atom-fixing power belonging to each, because the total atom-fixing power of two separate carbon atoms would be $4 + 4$, and if one atom-fixing power of each is employed in linking them together, the atom-fixing power of the chain would be $(4 - 1) + (4 - 1) = 6$.

If the two atoms were *doubly-linked* or united by two atom-fixing powers belonging to each, the atom-fixing power of the chain would be $(4 - 2) + (4 - 2) = 4$, expressed by C^{iv}_2.

Again, if the two atoms were *trebly-linked*, the atom-fixing power would be $(4 - 3) + (4 - 3) = 2$, expressed by C^{ii}_2.

So it is evident that each atom of carbon added to the chain can only increase the atom-fixing power of the chain itself by 2, for although the added atom of carbon has an atom-fixing power of 4, one of these must be used up in *attaching it to the chain*, and one of the atom-fixing powers of the chain must be used up in *attaching the chain to it.*

From these considerations it follows that *the total number of atoms of monad or triad elements united with carbon in an organic compound must be an even number*, because the atom-fixing power of the chain is always a multiple of 2, and no odd number of monad or triad elements could satisfy such an atom-fixing power.

Example.—Ultimate analysis gives CH_3O as the empirical formula for glycol, but this is evidently an impossible formula, since the atom-fixing powers are 4 belonging to the carbon, 3 belonging to the hydrogen, and 2 to the oxygen. The molecular formula of glycol is $C_2H_6O_2$, where the hydrogen atoms are an even number, the two carbon atoms being singly linked, C^{vi}_2, four of the six atom-fixing powers being used for the attachment of four of the hydrogen-atoms, and the other two for each of the oxygen atoms, the second atom-fixing power of each (diad) oxygen atom being used for the attachment of each of the remaining hydrogen atoms.

317. The determination of the molecular formula of a substance is seldom possible without determining the *rational* or *structural formula* which shows how the elements are really linked together in the formation of the compound. This is the highest branch of organic chemistry, and involves the careful study of the reactions of the substance with a view to ascertain which of the elements are linked together in such a manner as to form groups which may be exchanged for other groups, or elements, derived from other compounds. It is thus that the synthesis or artificial production of organic substances has, in many cases, been arrived at.

Example. Determination of the rational or structural formula of alcohol.—The molecular formula of alcohol deduced from its ultimate analysis and vapour-density was C_2H_6O. Are the elements all united so as to form one indivisible body or are they united in groups, so that the alcohol may be said to be divisible into parts? When sodium is placed in alcohol, it is dissolved with evolution of much hydrogen, and the alcohol is converted into a crystalline substance called sodium ethylate, which has the composition C_2H_5ONa. Comparing this with the formula of alcohol, it is seen that one atom of hydrogen is on a different footing from the other five, since it is capable of being displaced by Na. This would be expressed by writing the formula C_2H_5OH.

Again, when alcohol is acted on by hydrochloric acid gas, and distilled at a low temperature, it yields water and a very volatile liquid known as ethylic chloride, having the composition C_2H_5Cl. This decomposition would be expressed by the equation, $C_2H_5OH + HCl = C_2H_5Cl + HOH$, from which it is evident that the Cl of the HCl has been exchanged for OH in the alcohol, leading to the conclusion that alcohol is made up of at least two separate groups, and that one way of writing its rational formula is $C_2H_5.OH$.

It is the existence of such groups of elements which accounts for the production of so vast a number of organic compounds from the four elements C, H, N, and O, whereas inorganic compounds are formed by the different combinations of about 70 elements. The groups into which the four organic elements may be arranged may be regarded, in some sense, as new elements, and they are often referred to as *quasi-elementary bodies* or *organic radicals*.

318. An *organic radical* may be defined as a group of elements which appears unchanged in the products of a reaction, and is therefore found on both sides of the equation.

The following examples of such radicals may be usefully committed to memory:—

Hydroxyle*	occurring in	Alcohols and phenols	HO
Carboxyle	,,	Acids	CO_2H
Carbonyle	,,	Ketones	CO
Cyanogen	,,	Cyanogen compounds	CN
Nitroxyle	,,	Nitro-compounds	NO_2
Sulphonyle	,,	Sulphonic acids	$SO_2.OH$
Amidogen	,,	Amides	NH_2
Methyle	,,	Wood-spirit derivatives	CH_3
Ethyle	,,	Alcohol ,,	C_2H_5
Amyle	,,	Potato-spirit ,,	C_5H_{11}
Phenyle	,,	Benzene ,,	C_6H_5
Tolyle	,,	Toluene ,,	C_6H_4
Acetyle	,,	Acetic ,,	C_2H_3O
Benzoyle	,,	Benzoic ,,	C_7H_5O

319. By investigating the nature of the radicals contained in an organic substance, it may generally be assigned to one of the following divisions—

(1) HYDROCARBONS, composed of carbon and hydrogen only, in various modes of grouping; as *ethyl-hydride* or *ethane*, $C_2H_5.H$.

(2) ALCOHOLS, composed of carbon, hydrogen, and oxygen, and containing one or more *hydroxyle* (HO) groups; as *ethyl-alcohol*, $C_2H_5.HO$.

(3) ALDEHYDS, or dehydrogenated alcohols; products of the partial oxidation of the alcohols, containing the group (CO.H); as *ethyl-aldehyd* $CH_3.CO.H$.

(4) ACIDS, the products of the further oxidation of the alcohols, containing one or more *carboxyle* or *oxatyle* groups, CO_2H; as *acetic acid*, $CH_3.CO.OH$ or $CH_3.CO_2H$.

(5) KETONES, formed from the acids by the substitution of a hydrocarbon radical for the OH in the carboxyle; so that the ketones contain the group CO, like the aldehyds; as *acetic ketone* or *acetone*, $CH_3.CO.CH_3$.

(6) ETHERS, formed from the alcohols by the substitution of a compound radical for the H in the hydroxyle, as *ethyl-ether*, $C_2H_5.O.C_2H_5$.

(7) HALOID COMPOUNDS, formed from the alcohols or acids by the substitution of a halogen radical for the hydroxyle; as *ethyle chloride*, C_2H_5Cl; *acetyle chloride*, $CH_3.CO.Cl$.

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* The ending *-yle* is generally given to the names of organic radicals, because ὕλη is put for the *matter* of which a thing is made. The customary omission of the final *e* obscures the derivation.

(8) ETHEREAL SALTS (or *esters*), formed from the acids by the substitution of a compound radical for the hydrogen in the oxatyle group; as *ethyl acetate*, $CH_3.CO.OC_2H_5$.

(9) AMMONIA-DERIVATIVES, formed upon the model of ammonia, NH_3, by the substitution of a compound radical for hydrogen; as *ethylamine*, $NH_2.C_2H_5$, *acetamide*, $NH_2.C_2H_3O$.

(10) CYANOGEN COMPOUNDS, containing the group CN; as *hydrocyanic acid*, H.CN.

(11) PHENOLS, resembling the alcohols in composition, by containing the hydroxyle group, but resembling the acids in some of their properties, and not yielding aldehyds when partially oxidised; as *phenol*, $C_6H_5.OH$.

(12) QUINONES, formed from hydrocarbons by the substitution of a group of two oxygen atoms for two hydrogen atoms; as *quinone*, $C_6H_4(O_2)$, from benzene C_6H_6.

(13) ORGANO-MINERAL COMPOUNDS, formed upon the type of the chlorides of metals or non-metals by the substitution of organic radicals for the chlorine; as *zinc ethide*, $Zn(C_2H_5)_2$.

In cases where sufficient evidence has not been obtained as to the rational formulæ of compounds, they are classified according to their similarity in properties or in ultimate composition, or in products of decomposition. The following are the most important of such classes—

(14) CARBOHYDRATES, or compounds containing six, or some multiple of six, atoms of carbon, together with some multiple of the group, H_2O; as *starch*, $C_6H_{10}O_5$, *glucose*, $C_6H_{12}O_6$, *sugar*, $C_{12}H_{22}O_{11}$.

(15) GLUCOSIDES, or compounds which yield glucose as one of their products of decomposition; as *salicin*, $C_{13}H_{18}O_7$.

(16) ALBUMINOIDS and GELATINOIDS, or compounds containing C, H, N and O, often with small quantities of S, and sometimes of P, distinguished by their tendency to putrefy when moist; *albumen*, *fibrin*, and *casein* are examples of such compounds, but they cannot at present be represented by satisfactory formulæ.

Before attempting to study the inner structure of the molecules of organic bodies and the mechanism of their chemical action upon each other, it will be desirable to consider empirically the natural sources from which they are derived, and the artificial methods of obtaining them, as well as the chief properties which render them useful to the manufacturer or the chemist.

320. HYDROCARBONS.—The simplest of the hydrocarbons, CH_4, is known by the names *marsh-gas*, *fire-damp*, or *methane*, and is only too abundant in coal-mines, existing in a highly compressed state in the seams of coal, and escaping when the pressure is removed. It is believed to have been produced during the decomposition of the vegetable remains from which the coal was formed, because it is found among the gases evolved by the fermentation of vegetable matter. It is also produced in the distillation of coal, and constitutes nearly half the volume of coal-gas.

Preparation of marsh-gas.—Sodium acetate is heated with a mixture of caustic soda and slaked lime, $NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4$. The lime is added chiefly to render the mixture less fusible. The gas thus obtained contains hydrogen and acetone vapour. To prepare pure methane, methyle iodide is acted on by the copper-zinc couple (see p. 16) in presence of water or alcohol ; $CH_3I + HOH + Zn = CH_3H + ZnI.OH$. It may also be obtained by the action of sodium amalgam on carbon tetrachloride in the presence of water ;

$$CCl_4 + 4Na_2 + 4HOH = CH_4 + 4NaCl + 4NaOH.$$

The mercury is used to moderate the violent action of the sodium.

Properties of marsh-gas.—Nearly inodorous ; its sp. gr. is only 0.56, whence it was formerly called *light carburetted hydrogen.* It burns with a pale flame, is almost insoluble in water, but dissolves in twice its volume of alcohol. It has been liquefied by 180 atm. pressure at −11°.*

When mixed with chlorine and exposed to sunlight, a violent reaction occurs, and often an explosion, HCl being formed and C separated ; but when the Cl is diluted with CO_2 and allowed to act gradually, *chlorine-substitution-products* are obtained.

$CH_4 + Cl_2 = HCl + CH_3Cl$ *monochloromethane*
$CH_4 + 2Cl_2 = 2HCl + CH_2Cl_2$ *dichloromethane*
$CH_4 + 3Cl_2 = 3HCl + CHCl_3$ *chloroform*
$CH_4 + 4Cl_2 = 4HCl + CCl_4$ *tetrachloromethane*

The Cl in these compounds is not precipitated by silver nitrate like the Cl in HCl and the chlorides of the metals.

Methane is the first member of the important series of *paraffin hydrocarbons*, so named after a wax-like substance obtained in the distillation of coal and peat, which resisted the action of most chemical agents and was therefore deemed to have little chemical attraction or *affinity* (*parum, affinis*) for other bodies.

The paraffin hydrocarbons all contain C and H in the proportion expressed by the formula C_nH_{2n+2}, where n represents any whole number.

They constitute the greater portion of the liquids known as *petroleums* and *paraffin oils*.

Petroleum, or *rock oil*, has been known from a very early period, though it has but recently come into general use. It is found in nearly all countries, but especially at Baku, on the Caspian Sea, and in Canada and Pennsylvania, and occurs in almost all geological formations.

The *oil wells* discharge large volumes of gas containing H, CH_4, and C_2H_6 (*ethane*), which are used for heating and lighting in the neighbouring district.

The liquid pumped out of the wells still retains a quantity of ethane in solution. It consists chiefly of members of the paraffin series, of which a list is here given—

Methane	CH_4	gas
Ethane	C_2H_6	,,
Propane	C_3H_8	,,
Butane	C_4H_{10}	,,
		Boils at
Pentane	C_5H_{12}	38° C.
Hexane	C_6H_{14}	70°

		Boils at
Heptane	C_7H_{16}	98° C.
Octane	C_8H_{18}	125°
Nonane	C_9H_{20}	148°
Decane	$C_{10}H_{22}$	168°
Dodecane	$C_{12}H_{26}$	202°
Hexadecane	$C_{16}H_{34}$	278°

When the petroleum is distilled, the hydrocarbons, ethane, propane, and butane, are evolved in the gaseous state ; these are collected and subjected to the action of a condensing pump, which liquefies a portion of them, yielding the liquid sold as *cymogene*, which is used in freezing machines, on account of the cold produced by its rapid evaporation. It consists chiefly of butane, C_4H_{10}. The liquid constituents of the petroleum are separated by the process of *fractional distillation*, which depends upon the difference in their boiling points. The portion which distils over below 76° C. consists chiefly of pentane and hexane, and is sold as *petroleum spirit*, or *petroleum ether*, and used for dissolving india-rubber, and for making varnishes. The next fraction of the distillate is chiefly *heptane*, and is sold for burning in paraffin-lamps, under the names *benzoline*, *paraffin oil*, or *mineral sperm oil*. The oils boiling below 76° C. are not safe for burning in ordinary lamps because they so easily evolve vapour, which forms an explosive mixture with air, and bursts the lamp.

---

* Liquid methane has the sp. gr. 0.415 at −164° C. and 737 mm. Bar.

The temperature at which the hydrocarbon evolves enough vapour to form an inflammable mixture with the air above it is termed its *flashing-point*. No paraffin oil is considered safe for burning, in England, which kindles from a flame brought near its surface when it is heated to 38° C. (100° F.) *in an open vessel*; a teacup placed in a basin of hot water in which a thermometer is plunged, answers for a rough test. In a closed vessel, where the vapour more rapidly accumulates in sufficient quantity, the flashing-point is much lower, and no oil is considered safe which kindles at or below 23° C. (73° F.) in a covered vessel when a flame is brought near its surface; a small beaker covered with a piece of tin plate having a small hole for introducing a match, may be placed in warm water for the *close test*.

That portion of the petroleum which distils over between 150° C., and 200° C., consists chiefly of *nonane* and *dodecane*, and is used for lubricating machinery.

At still higher temperatures, the liquid which distils over consists of *hexadecane* and other hydrocarbons richer in carbon. These form soft solids, like *vaselin*, those containing most carbon form the wax-like crystalline solids originally termed paraffin.

Ozokerite, or *mineral wax*, is imported from Galicia, Hungary, and Russia, for the manufacture of candles. It contains 85 per cent. of carbon and 15 of hydrogen, and, when purified from an oil useful for illuminating purposes, consists of a group of solid hydrocarbons of the marsh gas series, melting at 140° F.

Bog-butter, found in the Irish peat-mosses, is a similar body. Another mineral resembling this, found in New South Wales, contained 80.6 per cent. C, 5.6 H, 5.5 N, 1.6 O, and 6.7 of ash.

The paraffin hydrocarbons are also obtained by distilling certain minerals allied to coal, such as the *Torbane Hill mineral*, or *Boghead coal*, found at Bathgate, in Scotland. The *shale oils* are also mixtures of paraffins obtained by distilling bituminous shales.

321. On the small scale, the process of fractional distillation for the separation of liquids of different boiling-points is conducted in a retort (A, fig. 273) through the tubulus of which a thermometer (T) passes, to indicate the temperature at which the liquid boils. The first portion which distils over will, of course, consist chiefly of that liquid which has the lowest boiling-point; and if the receiver (R) be changed at stated intervals corresponding to a certain rise in the temperature, a series of liquids will be obtained, containing substances the boiling points of which lie within the limits of temperature between which the liquids were collected.

When these liquids are again distilled separately in the same way, a great part of each is generally found to distil over within a few degrees on either side of some particular temperature, which is the boiling point of the substance of which that liquid chiefly consists; and if the receivers be again changed at stated intervals, a second series of distillates will be obtained, the boiling points of which are comprised within a narrower range of temperature. It will be evident that, by repeated distillations, the original mixture will eventually be resolved into a number of liquids, each distilling over entirely at about one particular temperature which is the boiling point of its chief constituent.

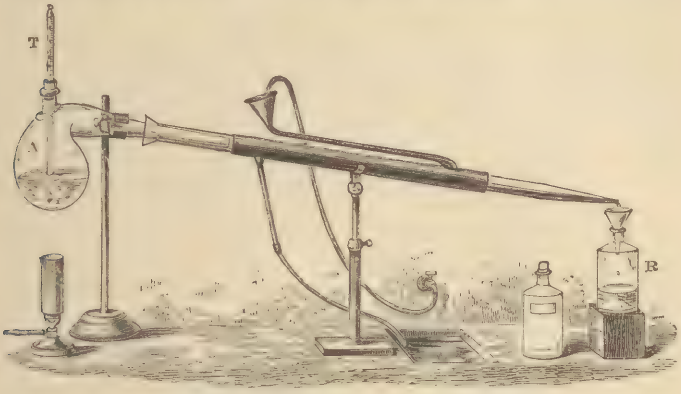

Fig. 273.—Fractional distillation.

A simple method of separating liquids which have different boiling points consists in distilling them in a flask (F, fig. 274) connected with a spiral worm (W) of glass or metal, surrounded by water or oil maintained at a temperature just above the boiling point of the particular liquid which is required to distil over. The greater part of the less volatile liquids will condense in the worm and run back into the flask. Thus, in extracting heptane from petroleum, the worm might be surrounded with boiling water, when the octane, &c. would be partly condensed in the worm, and the portion which passed into the receiver would consist chiefly of heptane.

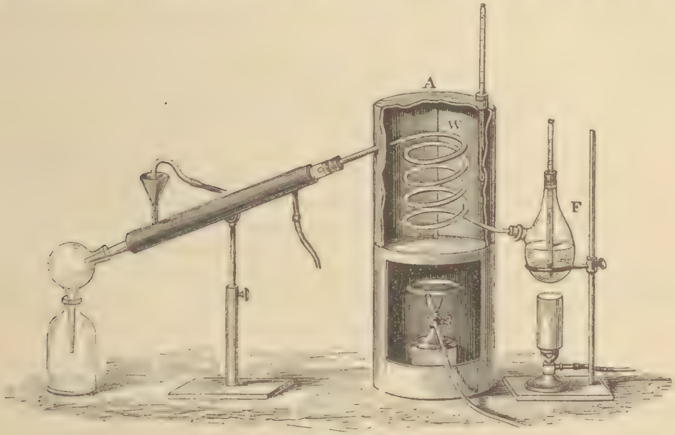

Fig. 274.—Refluxing condenser.

322. *Ethane*, C_2H_6, may be obtained artificially by heating methyl iodide with zinc in a sealed tube; $2CH_3I + Zn = ZnI_2 + C_2H_6$. Hence ethane is termed *dimethyl*. It resembles methane in properties but is more easily liquefied (46 atm.). It is about twice as soluble in alcohol as methane.

Propane, C_3H_8, is produced by the action of strong hydriodic acid (sp. gr. 1.9) upon glycerin at 275° C.; $C_3H_8O_3$ (*glycerin*) $+ 6HI = C_3H_8 + 3H_2O + 3I_2$. It is a gas which may be liquefied at about $-30°$ C. at the ordinary pressure.

Butane, C_4H_{10}, is made by acting on ethyl iodide with zinc (not in excess) in a sealed tube heated to 150° C.; $2C_2H_5I + Zn = ZnI_2 + C_4H_{10}$. It is much more easily condensed to a liquid than either of the preceding hydrocarbons, and is much more soluble in alcohol. Liquid butane boils at 1° C. and is the lightest known liquid, its sp. gr. being only 0.6.

Pentane, C_5H_{12}, occurs in the products of distillation of coal; it is liquid below 38° C. and very inflammable, burning with a luminous flame.

Hexane, C_6H_{14}, also found among the products from coal, may be obtained by the action of sodium on propyle iodide; $2C_3H_7I + Na_2 = 2NaI + C_6H_{14}$.

Heptane, C_7H_{16}, may also be obtained from coal-tar naphtha. It affords an example of a paraffin obtained directly from the vegetable kingdom, for it may be procured by distilling the exudation of the *Pinus sabiniana*, or nut-pine of California. It is used, under the name of *Abietene*, as a substitute for benzene in removing grease stains, &c.

Octane, C_8H_{18}, is a liquid prepared by decomposing butyl iodide with sodium; $2C_4H_9I + Na_2 = 2NaI + C_8H_{18}$.

Nonane, C_9H_{20}, has been little studied.

Decane, $C_{10}H_{22}$, is found among the products of the decomposition of the solid paraffins by heat.

Dodecane, $C_{12}H_{26}$, is a liquid obtained when potassium œnanthate ($KC_7H_{13}O_2$) in solution is decomposed by the galvanic current.

Hexadecane, $C_{16}H_{34}$, is a solid which fuses at 21° C. It has been obtained by the action of sodium amalgam on octyl iodide in the presence of water—

$$2C_8H_{17}I + Na_2 = 2NaI + C_{16}H_{34}$$

(HI would be formed, as an intermediate stage, by the nascent H from the H_2O).

There is some reason to believe that hexadecane is one of the components of *attar of roses*.

323. *Olefiant gas*, *ethylene*, or *ethene*, C_2H_4, is obtained by the action of powerful dehydrating agents on alcohol; $C_2H_5.OH = C_2H_4 + HOH$. It may be prepared by heating alcohol with twice its volume of strong sulphuric acid; secondary changes cause a carbonisation of the mixture, and the ethene is accompanied by some ether vapour, and by carbonic and sulphurous acid gases; the ether may be removed by passing it through strong sulphuric acid, and the acid gases by potash or soda.

Properties of ethene.—It has a faint ethereal odour, sp. gr. 0.97, and is liquefied at −110° C. Slightly soluble in water; more soluble in alcohol. Burns with a bright luminous flame, which renders it very useful as an illuminating constituent of coal-gas. When mixed with chlorine, ethene combines with it to form a fragrant liquid known as *ethene dichloride* or *Dutch liquid*, $C_2H_4Cl_2$. Bromine forms a similar compound with it. Sulphuric acid slowly absorbs ethene, forming $C_2H_5HSO_4$, *sulphethylic* or *sulphovinic acid*, from which alcohol may be obtained by distillation with much water;

$$C_2H_5HSO_4 + H_2O = C_2H_5HO + H_2SO_4.$$

Sulphuric anhydride absorbs ethene much more easily, and a strong solution of SO_3 in H_2SO_4 (fuming sulphuric acid) is employed for absorbing it in the analysis of coal-gas. The compound formed by SO_3 with ethene is crystalline, and is termed *carbyl sulphate* or *ethionic anhydride*, $C_2H_4(SO_3)_2$. In contact with water, it forms *ethionic acid*, $H_2C_2H_4S_2O_7$, and when this is boiled with water it yields *isethionic acid*, $H_2C_2H_4S_2O_7 + H_2O = H_2SO_4 + HC_2H_5SO_4$. It will be noticed that isethionic acid has the same composition as sulphethylic acid, but it is a more stable compound.

In presence of platinum-black, ethene combines with hydrogen to form ethane, C_2H_6.

Oxidising agents, such as nitric and chromic acids convert ethene into oxidised bodies containing two carbon atoms, such as oxalic acid, $C_2H_2O_4$, aldehyd, C_2H_4O, and acetic acid, $C_2H_4O_2$.

From the above description of the properties of ethene, it will be seen that it differs greatly from methane and the other paraffins, in the readiness with which it combines with other bodies, especially with chlorine, bromine, and sulphuric anhydride.

Ethene is the first member of the series of hydrocarbons known as *olefins*, which contain twice as many atoms of H as of C, so that the general formula of the series is C_nH_{2n}, where n represents any whole number not less than 2.

They are found in the products of distillation of coal, wood, &c. The following is a list of the chief members of the olefin series—

					Boils at
Ethylene	C_2H_4	Gas.	Caprylene	C_8H_{16}	125° C.
Propylene	C_3H_6	,,	Elaene	C_9H_{18}	
Butylene	C_4H_8	,,	Diamylene	$C_{10}H_{20}$	158°
		Boils at	Hendecatene	$C_{11}H_{22}$	200°
Amylene	C_5H_{10}	35° C.	Cetylene	$C_{16}H_{32}$	275°
Hexylene	C_6H_{12}	70°	Cerotene	$C_{27}H_{54}$	
Heptylene	C_7H_{14}	100°	Melissene	$C_{30}H_{60}$	

Propylene, or *propene*, or *tritylene*, C_3H_6, occurs in small quantity in coal-gas, being one of the *illuminants*. It may be obtained by heating glycerin with zinc dust; $C_3H_5(OH)_3 + Zn_3 = C_3H_6 + H_2 + 3ZnO$. Its properties resemble those of ethylene, but it is, of course, half as heavy again, because $C_3H_6 = 42$ weights = 2 volumes, whereas $C_2H_4 = 28$ weights = 2 volumes. It is more easily absorbed by strong sulphuric acid.

Butylene, or *butene*, or *tetrylene*, C_4H_8, occurs largely in the illuminating gas made by distilling the vegetable and animal oils. It is also found in the odorous hydrocarbons which are evolved when cast iron is dissolved in hydrochloric or dilute sulphuric acid. It condenses to a liquid at about − 10°.

Amylene, or *pentene*, C_5H_{10}, is obtained by heating amyl alcohol (*fousel oil*) with zinc chloride, which acts as a dehydrating agent; $C_5H_{11}.OH = C_5H_{10} + H_2O$. It is accompanied by *diamylene*, $C_{10}H_{20}$; *triamylene*, $C_{15}H_{30}$; and *tetramylene*, $C_{20}H_{40}$. Amylene occurs in petroleums and paraffin oils. It is a liquid of sp. gr. 0.66, boiling at 35° C. Commercial amylene is a mixture of several hydrocarbons having the same composition.

The remaining members of the olefin series have little practical importance.

324. *Acetylene* or *ethine*, C_2H_2, is the only hydrocarbon which can be formed by the direct union of its elements. It is produced when carbon is very strongly heated in hydrogen, by passing a powerful electric current, such as is used for electric lighting, between two carbon terminals surrounded by a globe filled with hydrogen.

This act of combination is remarkable for being attended by absorption instead of evolution of heat, to the amount of 61,100 units; so that the sudden decomposition of acetylene should evolve enough heat to raise the temperature to 3,000°, which would so expand the liberated hydrogen as to cause an explosion. Accordingly, it is found that the intense molecular vibration produced by detonating a minute quantity (a decigramme) of mercuric fulminate in 25 cubic centimetres of acetylene, causes the latter to detonate violently, yielding hydrogen and finely divided carbon.

Acetylene is a constant product of the destructive distillation and imperfect combustion of bodies rich in carbon and hydrogen.

Pure acetylene may be prepared by heating ethene dibromide with caustic potash dissolved in alcohol;

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

Properties of acetylene.—A gas of peculiar odour, and sp. gr. 0.91. It becomes liquid at 1° C. under a pressure of 48 atmospheres. Water at

18° C. dissolves its own volume of the gas, hence it may be collected over water, but with some loss. It burns with a brighter flame than olefiant gas, but emits smoke. In the presence of platinum-black it combines with hydrogen to form ethene, C_2H_4. Strong sulphuric acid absorbs acetylene slowly, as it does ethene; but when the solution is mixed with water and distilled, it yields, not alcohol as with ethene, but *croton-aldehyd*, $C_3H_5.COH$; $2C_2H_2 + H_2O = C_4H_6O$. Chromic acid oxidises acetylene to acetic acid; $C_2H_2 + H_2O + O = C_2H_4O_2$. A mixture of potassium permanganate with potash converts it into oxalic acid;

$$C_2H_2 + O_4 = C_2H_2O_4.$$

The most remarkable feature of acetylene is the facility with which its hydrogen is displaced by metals. By heating sodium in acetylene, C_2HNa, *mono-sodium acetylide* and C_2Na_2, *di-sodium acetylide* may be obtained. *Cuprous acetylide*, $C_2Cu_2.H_2O$ is formed when acetylene acts upon a cuprous compound in the presence of ammonia; thus, if acetylene be passed into an ammoniacal solution of cuprous chloride;

$$Cu_2Cl_2 + 2NH_3 + C_2H_2 = C_2Cu_2 + 2NH_4Cl.$$

The cuprous acetylide forms a bright-red precipitate, the production of which forms a characteristic test for acetylene. As might be expected from the behaviour of acetylene itself, the copper compound is exploded by heat or by percussion, and its formation has caused accidents in copper or brass pipes through which coal-gas containing ammonia has been passed.

Silver acetylide, $C_2Ag_2.H_2O$, is produced as a white precipitate when acetylene is passed into silver nitrate, or when a little ether is poured upon solution of silver nitrate in a test-tube, at the mouth of which the ether is then kindled, when its imperfect combustion inside the tube produces acetylene. Silver acetylide is more explosive than the copper compound.

Acetylene inflames at once on contact with chlorine in daylight, yielding HCl and finely divided carbon; but if acetylene be passed into antimonic chloride, kept cool, crystals of $C_2H_2Cl_2.SbCl_3$ are formed, which, on heating, yield the *acetylene dichloride*, $C_2H_2Cl_2$, as a liquid smelling like chloroform, and boiling at 55° C. $C_2H_2Cl_4$, *acetylene tetrachloride* and C_2HCl, *monochloracetylene*, have also been obtained.

When heated in a sealed tube, acetylene is partially converted into a mixture of two liquids, *benzene*, C_6H_6 and *styrolene*, C_8H_8. By passing electric sparks through a mixture of acetylene with nitrogen, *hydrocyanic acid* is produced; $C_2H_2 + N_2 = 2HCN$. Hence this acid, from which a large number of organic bodies may be derived, has been synthesised from its elementary constituents. Cuprous acetylide, in contact with zinc and solution of ammonia, yields ethylene, which is convertible into alcohol, and from this a very large number of organic compounds may be made.

Acetylene is regarded as one of the most important intermediate bodies in the synthesis of organic compounds from their elements.

Acetylene is the first member of the *acetylene series* of hydrocarbons which contain carbon and hydrogen in the proportions expressed by the general formula, C_nH_{2n-2}, where n represents any whole number not less than 2.

The chief members of the series which have been studied are:*—

---

* Schorlemmer.

Acetylene	C_2H_2	Gas.			Boils at
Allylene	C_3H_4	,,	Œnanthylidene	C_7H_{12}	107° C.
		Boils at	Caprylidene	C_8H_{14}	133°
Crotonylene	C_4H_6	18° C.	Decenylene	$C_{10}H_{18}$	165°
Valerylene	C_5H_8	45°	Benylene	$C_{15}H_{28}$	225°
Hexoylene	C_6H_{10}	80°	Cetenylene	$C_{16}H_{30}$	280°

Allylene, or *propine*, C_3H_4, resembles acetylene, but its cuprous compound is yellow instead of red.

Crotonylene, or *butine*, C_4H_6, is a liquid; its vapour is one of the illuminating hydrocarbons in coal-gas.

The other members of the series have no practical importance at present.

325. It will have been noticed that the paraffins, olefins, and acetylenes increase regularly by CH_2. Since the general formulæ of the three series are, respectively, C_nH_{2n+2}, C_nH_{2n} and C_nH_{2n-2}, there are three hydrocarbons containing C_2, viz., *ethane* C_2H_6, *ethene*, C_2H_4, and *ethine*, C_2H_2, and, starting from these, and adding regularly CH_2, the three series are formed

Paraffins.	Olefins.	Acetylenes.
CH_4	...	...
C_2H_6	C_2H_4	C_2H_2
C_3H_8	C_3H_6	C_3H_4
C_4H_{10}	C_4H_8	C_4H_6
C_5H_{12}	C_5H_{10}	C_5H_8
&c.	&c.	&c.

The series in each vertical column is said to be *homologous* because it increases by the regular addition of CH_2; whilst the series in each horizontal line is said to be *isologous*, because its members contain an equal number of carbon atoms.

The formation of these series will be explained hereafter.

326. *Benzene*, C_6H_6, occurs in petroleum, but is more abundant in the *light oil* obtained in the distillation of coal-tar. From this it is obtained by fractional distillation; the portion which distils between 79° and 82° C. consists chiefly of benzene, and is purified by cooling it below 0° C. when the benzene crystallises, while the other hydrocarbons remain liquid and are removed by pressure.

Properties of benzene.—It is an ethereal liquid, having the odour of coal-gas, of which benzene vapour is one of the illuminating constituents. It has the sp. gr. 0.878, freezes at 0° C. and boils at 81° C. It is very inflammable, and burns with a red smoky flame; but its vapour, when mixed with air or hydrogen (as in coal-gas), burns with a bright white flame. Benzene is insoluble in water, but dissolves in alcohol and ether. It is largely used for dissolving fats, caoutchouc, &c. If benzene be dropped into the strongest nitric acid, or into a mixture of ordinary concentrated nitric acid with an equal volume of strong sulphuric acid, a violent action is set up, red fumes are evolved, and the liquid becomes red. On pouring it into several times its volume of water, a heavy, oily liquid falls, which is *nitrobenzene*, $C_6H_5NO_2$;

$$C_6H_6 + NO_2.OH = C_6H_5NO_2 + H_2O.$$

The red fumes result from a secondary reaction not expressed in the equation. The sulphuric acid is used to combine with the water, since weak nitric acid does not act on benzene. Nitrobenzene has a powerful odour of almonds, and is sold, dissolved in alcohol, as *Mirbane essence*, for use in confectionery and perfumery. It is, however, a poisonous substance in large doses. It is also largely employed for the preparation of aniline. Nitrobenzene boils at 220° C.

If the mixture of nitric and sulphuric acids be boiled with the benzene, the liquid deposits, on cooling, a yellowish crystalline solid which is *dinitrobenzene*, $C_6H_4(NO_2)_2$;

$$C_6H_6 + 2(NO_2.OH) = C_6H_4(NO_2)_2 + 2H_2O.$$

Strong sulphuric acid also oxidises part of the hydrogen in benzene, when heated with it, leaving in its place the *sulphonic group*, or *sulphuric acid residue*, $SO_2.OH$, which bears the same relation to sulphuric acid, $SO_2(OH)_2$, as nitroxyle, NO_2, bears to nitric acid, $NO_2.OH$; thus $C_6H_6 + SO_2(OH)_2 = H_2O + C_6H_5.SO_2.OH$ (*benzene-sulphonic acid*). If fuming sulphuric acid be used, a second atom of hydrogen may be replaced; $C_6H_6 + 2SO_2(OH)_2 = 2H_2O + C_6H_4(SO_2.OH)_2$ (*benzene-disulphonic acid*).

When chlorine is passed into benzene (containing a little iodine which assists the reaction), *monochlorobenzene*, C_6H_5Cl, is formed; it is an almond-smelling liquid, which boils at 138° C., is not decomposed by caustic alkalies, and is reconverted into benzene by water and sodium-amalgam (to yield nascent hydrogen). The further action of chlorine on benzene yields

Dichlorobenzene, $C_6H_4Cl_2$
Trichlorobenzene, $C_6H_3Cl_3$
Tetrachlorobenzene, $C_6H_2Cl_4$
Pentachlorobenzene, C_6HCl_5
Hexachlorobenzene, C_6Cl_6

These are all crystalline solid bodies.

Beside these *substitution-products*, benzene is capable of forming *addition-products* with chlorine; *benzene dichloride*, $C_6H_6Cl_2$; *tetrachloride*, $C_6H_6Cl_4$; *hexachloride*, $C_6H_6Cl_6$. These are less stable than the substitution-products; thus, the hexachloride, when heated with potash dissolved in alcohol, yields trichlorobenzene;

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O.$$

When benzene is treated with hydric peroxide, it is slowly converted into *hydroxybenzene* or *phenol*; $C_6H_6 + H_2O_2 = C_6H_5.OH + H_2O$.

Benzene was so called because it was first prepared by distilling benzoic acid with (3 parts) slaked lime;

$$C_6H_5.CO_2H + Ca(OH)_2 = C_6H_6 + CaCO_3 + H_2O.$$

Coal-tar benzene generally contains a small quantity of a compound termed *thiophene*, C_4H_4S, a liquid boiling at 84° C., characterised by forming an intensely blue substance, *indophenin*, $C_{12}H_7NOS$, when in contact with isatin and strong sulphuric acid. Thiophene is formed when olefiant gas is passed through sulphur at the boiling point. Some of its derivatives closely resemble those from benzene. It has been produced artificially by acting on sodium succinate with phosphorus sulphide.

327. Benzene is the first member of a series of homologous hydrocarbons, known as the *benzene series* or *aromatic hydrocarbons*, represented by the general formula C_nH_{2n-6}, in which n may be any whole number not less than 6.

The principal hydrocarbons of the benzene series are the following:—

		Boils at			Boils at
Benzene	C_6H_6	81° C.	Pseudocumene	C_9H_{12}	166° C.
Toluene	C_7H_8	111°	Durene	$C_{10}H_{14}$	190°
Xylene	C_8H_{10}	140°	Amyl-toluene	$C_{12}H_{18}$	213°

These hydrocarbons (except the two last) are extracted from the coal-tar obtained by the distillation of coal for the manufacture of coal-gas. A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown oily offensive liquid which collects upon the surface of the water. This is the *light oil* containing the benzene hydrocarbons. To purify it, it is shaken with caustic soda, to dissolve carbolic acid (phenols), and afterwards with sulphuric acid which removes aniline and other basic compounds. It is then subjected to the process of fractional distillation described at p. 470.

Toluene, C_7H_8, or *methyl-benzene*, $C_6H_5CH_3$, is always present in commercial benzene. It was originally distilled from balsam of Tolu, and may be prepared by distilling *toluic acid*, $C_7H_7.CO_2H$, with lime. It is a little heavier than benzene (sp. gr. 0.882) which it resembles in odour, but it does not solidify even at $-20°$ C. Benzene may be converted into toluene by first obtaining *bromobenzene*, C_6H_5Br, and treating this with methyl iodide and sodium, in the presence of ether—

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaBr + NaI.$$

Under the action of oxidising agents, toluene yields benzoic acid.*

When acted on by sulphuric acid, toluene yields *toluene-sulphonic acid*, $C_6H_4.CH_3.SO_2.OH$. The corresponding amide, *toluene-sulphonamide*—

$$C_6H_4.CH_3.SO_2.NH_2,$$

when oxidised by potassium permanganate, yields a compound having the formula, $C_6H_4.CO.SO_2.NH$, which has been named *saccharine*, on account of its sweet taste, which far exceeds that of sugar. It is soluble in water, alcohol, and ether, and fuses at 220° C. with partial decomposition. When fused with potash, it is converted into potassium salicylate.

Xylene, C_8H_{10}, or *dimethyl-benzene*, $C_6H_4(CH_3)_2$, is a liquid of unpleasant odour.

Durene, $C_{10}H_{14}$, or *tetramethyl-benzene*, $C_6H_2(CH_3)_4$, is a crystalline solid, fusing at 80° C. It is lighter than water, which does not dissolve it; it is soluble in alcohol.

Amyl-toluene, $C_{12}H_{18}$, or $C_7H_7.C_5H_{11}$, is a liquid obtained by acting upon bromotoluene with amyl bromide and sodium—

$$C_7H_7Br + C_5H_{11}Br + Na_2 = C_7H_7.C_5H_{11} + 2NaBr.$$

Hexamethyl-benzene, $C_6(CH_3)_6$, has the same percentage composition as amyltoluene, but it is a crystalline solid, fusing at 150° C. and boiling at 260°.

328. The *methyl substitution-products* of benzene are formed by a process which has not yet been satisfactorily explained. Benzene is not acted on by methyl chloride, nor by aluminium chloride, Al_2Cl_6, but if the latter be dissolved in hot benzene, and methyl chloride vapour be passed into it, HCl is evolved and the benzene is converted into toluene (methyl-benzene; $C_6H_6 + CH_3Cl + Al_2Cl_6 = C_6H_5.CH_3 + HCl + Al_2Cl_6$. The action of the methyl chloride may be carried further, so as to displace successively each of the six hydrogen atoms of the benzene, the hexamethyl-benzene being the final product.

The benzene series is remarkable for containing a large number of hydrocarbons which have the same percentage composition and the same molecular weight, and are yet very different in their properties, because their rational formulæ are different. Such bodies are said to be *isomeric* or *metameric*.

Isomeric bodies or *isomerides* are those which have the same percentage composition and the same molecular weight. *Metameric* bodies have the same percentage composition and molecular weight, but have different rational formulæ. *Polymeric* bodies, or *polymerides*, have the same percentage composition, but different molecular weights.

The theoretical explanation of the difference in properties between bodies containing the same elements in the same proportions will be given hereafter.

329. *Cinnamene*, or *styrolene*, C_8H_8, is obtained by distilling cinnamic acid with lime; $C_8H_7.CO_2H + Ca(OH)_2 = C_8H_8 + CaCO_3 + H_2O$. It can also be prepared by distilling balsam of storax, or by distilling the resin known as dragon's blood with zinc-dust. Cinnamene is a fragrant liquid of sp. gr. ·924, and boiling point 145° C. It resembles the olefin hydrocarbons in uniting directly with chlorine, bromine and iodine. When heated in a sealed tube to 200° C., it becomes converted into a transparent solid known as *metacinnamene*, or *metastyrolene*, which is polymeric with cinnamene, into which it is reconverted by distillation.

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* Toluene is formed in large proportion when heptine (œnanthylidene, C_7H_{12}) is dropped into a red-hot iron tube.

When heated with hydrochloric acid to 170° C., cinnamene is converted into *di-cinnamene*, $C_{16}H_{16}$.

When acted on by strong nitric acid, cinnamene yields *nitrocinnamene*, $C_8H_7NO_2$, which is not liquid like nitrobenzene and nitrotoluene, but crystallises in prisms.

The *cinnamene series* of hydrocarbons has the general formula C_nH_{2n-8}, but very few members of it are known.

Other examples of these hydrocarbons are *phenyl-propylene*, C_9H_{10}, or $C_3H_5.C_6H_5$ and *phenyl-butylene* $C_{10}H_{12}$ or $C_4N_7.C_6H_5$. Cinnamene itself is *phenyl-ethylene*, $C_2H_3.C_6H_5$, which accounts for the resemblance between the cinnamenes and olefins.

330. *Naphthalene*, $C_{10}H_8$, is a crystalline hydrocarbon with an odour of coal-gas, and is occasionally deposited in gaspipes in cold weather, causing an obstruction. It is a very common product of the action of a high temperature upon substances rich in carbon; coal and wood yield it on distillation; marsh gas, alcohol vapour and ether vapour, when passed through a red-hot tube, deposit crystals of naphthalene in the cooler part. Burmese petroleum and Rangoon tar contain naphthalene.

When coal-tar is distilled, the benzene hydrocarbons which distil over in the *light-oil*, are succeeded, as the temperature rises, by a yellow oil which is heavier than water. This, known as *dead-oil*, is much more abundant than the light-oil, amounting to about one-fourth of the weight of the tar, and containing those constituents of the tar which have a high specific gravity and boiling point. When the temperature has risen to about 200° C., the distilled liquid partly solidifies on cooling, from the crystallisation of naphthalene. This portion is pressed to expel the liquid part, and boiled with alcohol, which deposits the naphthalene as it cools. Or the crude naphthalene may be gently heated in an iron pot over which is inverted another vessel kept cool, in which the naphthalene sublimes in brilliant feathery crystals.

Properties of naphthalene.—Transparent crystals, smelling of gas, very fusible, at 80° C., and inflammable, burning with a smoky flame. It sublimes much below its boiling point (217° C.). Insoluble in water, soluble in alcohol, ether and benzene.

In its chemical relations, naphthalene is closely connected with benzene, but it shows less disposition to form addition-products with chlorine and bromine, with which it yields numerous substitution-products. *Naphthalene*, however, absorbs chlorine, forming a yellow liquid, *naphthalene dichloride*, $C_{10}H_8Cl_2$, and a crystalline solid, *naphthalene tetrachloride* $C_{10}H_8Cl_4$. The non-existence of $C_{10}H_8Cl_3$ is in accordance with the law of even numbers (p. 446). When naphthalene tetrachloride is further acted on by chlorine, it yields $C_{10}H_7Cl_5$, and $C_{10}H_6Cl_6$, which may be regarded as $C_{10}H_8Cl_4$ in which one and two atoms of chlorine, respectively, have been substituted for hydrogen.

By distilling these chlorine compounds with an alcoholic solution of potash, the elements of HCl are removed, and substitution-products are obtained; thus $C_{10}H_8Cl_2 + KHO = C_{10}H_7Cl + KCl + H_2O$. The *monochloronaphthalene*, or *chlonaphtase*, $C_{10}H_7Cl$, which is thus obtained, is a colourless liquid boiling at 263° C. Naphthalene tetrachloride, treated in the same way, yields *dichloronaphthalene*, or *chlonaphtese*, $C_{10}H_6Cl_2$, as a crystalline solid. By similar methods, the substitution-products, $C_{10}H_5Cl_3$ (*chlonaphtise*), $C_{10}H_4Cl_4$ (*chlonaphtose*), $C_{10}H_2Cl_6$ (*chlonaphthalase*), and $C_{10}Cl_8$ (*chlonaphthalise*) have been obtained. Another method has also furnished $C_{10}H_3Cl_5$ (*chlonaphtuse*), so that only the compound $C_{10}HCl_7$ (*chlonaphthalese*) is missing. These are all crystalline solids.

The compound $C_{10}Cl_8$, *perchloronaphthalene*, is best obtained by acting on naphthalene with chlorine in the presence of antimonic chloride. It fuses at 135° C. and boils at 403°, whereas naphthalene, $C_{10}H_8$, fuses at 80° and boils at 218°. Bromine gives rise to similar products, and it is possible to replace part of the hydrogen in naphthalene by chlorine and part by bromine, yielding such compounds as the following:—

Chlorebronaphtise	$C_{10}H_5Cl_2Br$	*Bromachlonaphtose*	$C_{10}H_4BrCl_3$
Chlorebronaphtose	$C_{10}H_4Cl_2Br_2$	*Bromechlonaphtuse*	$C_{10}H_3Br_2Cl_3$.

The only iodine substitution derivative of naphthalene at present known is $C_{10}H_7I$, *moniodonaphthalene*, a colourless liquid, boiling at above 300° C. It is not obtained by the action of iodine on naphthalene.

The substitution-products derived from naphthalene have many isomerides, differing in properties according to the particular hydrogen atom which has been replaced by chlorine, bromine, or other radicals; the theoretical importance of this will be seen hereafter.

The *nitro-compounds* derived from naphthalene are more numerous than those from benzene.

Nitronaphthalene, $C_{10}H_7.NO_2$, is formed when nitric acid acts on naphthalene in the cold, but the action is much less violent than that on benzene. It is best prepared by adding nitric acid (sp. gr. 1.42) to naphthalene dissolved in glacial acetic acid and boiling for a short time. It forms yellow prismatic crystals which may be sublimed if heated carefully. It dissolves in alcohol.

Dinitronaphthalene, $C_{10}H_6(NO_2)_2$, is obtained by boiling naphthalene with strong nitric acid until it has entirely dissolved in the liquid. It is a colourless crystalline body which deflagrates when heated. It has an isomeride, β-dinitronaphthalene, which forms yellow plates more soluble in glacial acetic acid, and fusing at 170° C. instead of 211°. Nitronaphthalene fuses at 61°.

Trinitronaphthalene, $C_{10}H_5(NO_2)_3$, is obtained when dinitronaphthalene is boiled with fuming nitric acid; it forms tabular crystals exploding when heated. The prolonged action of the acid converts it into *tetranitronaphthalene*, $C_{10}H_4(NO_2)_4$, which forms yellow prisms.

These nitro-compounds have several isomerides.

When naphthalene is long boiled with dilute nitric acid, it is oxidised and converted into *naphthalic* or *phthalic acid*, $C_6H_4(CO_2H)_2$, and oxalic acid, $C_2H_2O_4$.

Naphthalene-sulphonic acid, $C_{10}H_7.SO_2.OH$, and *naphthalene-disulphonic acid*, $C_{10}H_6(SO_2.OH)_2$, are produced when naphthalene is heated with strong sulphuric acid.

Naphthalene behaves in a rather characteristic way with picric acid. If it be dissolved in hot alcohol and mixed with a hot solution of picric acid in alcohol, stellate tufts of yellow needles are deposited on cooling. These consist of a compound of single molecules of naphthalene and picric acid.

The general expression for the *naphthalene hydrocarbons* would be C_nH_{2n-12} but only two members of the homologous series are at present known; these are *methyl-naphthalene*, $C_{10}H_7.CH_3$ or $C_{11}H_{10}$, and *ethyl-naphthalene*, $C_{10}H_7.C_2H_5$ or $C_{12}H_{12}$. These are liquid even at low temperatures, and have little in common with naphthalene.

Ethene-naphthalene, or *acenaphthene*, $C_{10}H_6.C_2H_4$, which is found in small quantity in coal-tar, has been obtained by passing vapour of ethyl-naphthalene through a red-hot tube, when hydrogen is separated. A mixture of benzene vapour and ethene will also yield it in a similar way. It forms colourless prisms which fuse at 110° C. and boil at 268°. It is sparingly soluble in cold alcohol. Mixed with picric acid in hot alcoholic solution it deposits red needles.

Ethine-naphthalene, $C_{10}H_6.C_2H_2$, is obtained as a fusible solid (92° C.) by passing vapour of acenaphthene over red-hot lead oxide, which removes H_2.

Dinaphthyle, $C_{20}H_{14}$, is produced when vapour of naphthalene is passed through a red-hot tube; $2C_{10}H_8 = C_{20}H_{14} + H_2$. It is also formed by the oxidising action of MnO_2 with H_2SO_4 on naphthalene. It is best prepared by decomposing bromonaphthalene with sodium; $2C_{10}H_7Br + Na_2 = C_{20}H_{14} + 2NaBr$. It forms scaly crystals fusing at 154° C. and afterwards subliming.

331. *Anthracene*, $C_{14}H_{10}$, or *paranaphthalene*, is found among the last products of the distillation of coal-tar (especially from Newcastle coal), and may be distinguished from naphthalene by its being almost insoluble in alcohol, and

fusing only at 213° C., while naphthalene fuses at 80°. That fraction of the coal-tar distillate which comes over at about 360° C. solidifies on cooling to a mass of crude anthracene. It is freed from liquid hydrocarbons by pressure, washed with carbon disulphide, and purified by crystallisation from hot benzene, or by sublimation as for naphthalene. Commercial anthracene is employed for the manufacture of alizarin.

Anthracene is formed when vapour of toluene is passed through a red-hot tube containing pumice-stone to expose a large heated surface; $2C_7H_8 = C_{14}H_{10} + 3H_2$. Lead oxide, by oxidising the H, effects the change at a lower temperature.

Anthracene forms yellowish tabular crystals having a blue fluorescence. It has a very high boiling point (above 360° C.), and is therefore difficult of sublimation. It absorbs chlorine, forming crystals of *anthracene dichloride*, $C_{14}H_{10}Cl_2$, and *chloranthracene*, $C_{14}H_9Cl$.

Dichloranthracene, $C_{14}H_8Cl_2$, *tetrachloranthracene*, $C_{14}H_6Cl_4$, and the corresponding bromine compounds are also known.

By acting on dibromanthracene with bromine, *dibromanthracene tetrabromide*, $C_{14}(H_8Br_2)Br_4$, is obtained, and this, when heated, yields *tribromanthracene*, $C_{14}H_7Br_3$.

With nitric acid, anthracene behaves in a different way from benzene and naphthalene, showing less disposition to the formation of nitro-compounds. When heated with nitric acid it undergoes oxidation and is converted into a yellow crystalline body called *anthraquinone*, $C_{14}H_8O_2$ or $(C_6H_4)_2(CO)_2$.

By the action of nitric acid upon anthracene in alcoholic solution, *nitro-anthracene*, $C_{14}H_9NO_2$, has been obtained in red needle-like crystals. It has a white isomeride which is more soluble in alcohol. *Dinitroanthracene*, $C_{14}H_8(NO_2)_2$, has been obtained in colourless crystals.

Anthracene has been obtained synthetically from benzene and acetylene tetra-bromide in presence of aluminium chloride; $2C_6H_6 + C_2H_2Br_4 = C_{14}H_{10} + 4HBr$.

When anthracene is heated with strong sulphuric acid to 100° C., it is converted into *anthracene-sulphonic acid*, $C_{14}H_9.SO_2.OH$; at a higher temperature, *anthracene-disulphonic acid*, $C_{14}H_8(SO_2.OH)_2$, is produced.

Para-anthracene, isomeric or polymeric with anthracene, is deposited in crystalline plates when a cold saturated solution of anthracene in benzene is exposed to sunshine. It does not fuse until heated to 244° C., when it is reconverted into anthracene. Bromine and nitric acid do not act upon it.

Another isomeride, *iso-anthracene*, is known, which has a blue fluorescence and fuses at 247° C., but is then converted into anthracene. Moreover, it is acted on by nitric acid, yielding nitro-compounds.

By heating anthracene with strong hydriodic acid and amorphous phosphorus, it may be converted into *di-hydro-anthracene*, $C_{14}H_{12}$, and *hexa-hydro-anthracene*, $C_{14}H_{16}$, crystalline solids, easily soluble in alcohol, and decomposed by heat into hydrogen and anthracene.

Phenanthrene, $C_{14}H_{10}$, isomeric with anthracene, also occurs among the last products of the distillation of coal-tar. It is more soluble in alcohol than anthracene, and fuses at about 100° C.

Pyrene, $C_{16}H_{10}$, and *chrysene*, $C_{18}H_{12}$, are obtained at the end of the distillation of coal-tar; they are crystalline solids, and have been also found among the products of distillation of fatty and resinous bodies. Pyrene contains more carbon (95 per cent.) than any other hydrocarbon, and even more than is to be found in coal itself.

Idrialene, $C_{22}H_{14}$, has been obtained from *idrialite*, a mineral resembling coal found in the Idrian mercury mines; it is extracted by benzene, from which it crystallises.

Retene, $C_{18}H_{18}$, is a crystalline hydrocarbon resembling naphthalene, distilled from wood-tar.

332. *Oil of turpentine*, $C_{10}H_{16}$, is obtained by distilling the viscous exudation procured by cutting into the bark of various species of pine. Several varieties of turpentine are met with in commerce, of which the two best known are the common turpentine which is obtained from the Scotch fir, and Venice turpentine from the larch. These are both solutions of *colophony*, or common rosin, in oil of turpentine, and when distilled, yield from 75 to 90 per cent. of rosin, which remains in the still,

and from 25 to 10 per cent. of the oil, commonly sold as *spirits of turpentine.*

The oil of turpentine boils at 156° C., and has the sp. gr. 0.864. It is very sparingly soluble in water, but dissolves in alcohol and ether. It burns with a smoky luminous flame. Its property of dissolving resins and fats renders it useful in preparing paints and varnishes. It is also a good solvent for caoutchouc.

When oil of turpentine is heated in a closed vessel to about 250° C. for some hours, it is converted into an isomeride, *iso-terebenthene*, boiling at 160° C., and a polymeride, *meta-terebenthene*, $C_{20}H_{32}$, boiling at 349° C.

The French turpentine, or *terebenthene*, from *Pinus maritima*, has the same composition as English turpentine, or *australene*, from *Pinus australis*, but they differ in their optical properties, the French oil being *lævorotatory*, or turning the plane of polarisation of a beam towards the left, whilst the English oil is *dextrorotatory*, or turns it to the right. This is an instance of *physical isomerism*, for the chemical properties of the two oils are identical.

In contact with cold sulphuric acid, turpentine is polymerised into *colophene* or *diterebene*, $C_{20}H_{32}$, which has the sp. gr. 0.94, boils at 316° C., and has an indigo-blue fluorescence.

The action of chlorine and bromine on turpentine has been but little studied; *tetrachloroterpene*, $C_{10}H_{12}Cl_4$, is a crystalline solid, and *terpene dibromide*, $C_{10}H_{16}Br_2$, is an oily liquid.

Iodine, added in small portions, and afterwards gently heated, converts turpentine into *cymene*; $C_{10}H_{16} + I_2 = C_{10}H_{14} + 2HI$. Cymene belongs to the benzene series of hydrocarbons.

Strong nitric acid inflames turpentine, but dilute nitric acid, when boiled with it, yields several acids by oxidation, viz., acetic, propionic, butyric, terebic, oxalic, &c.

The action of hydrochloric acid on turpentine is characteristic. When HCl gas is passed into turpentine well cooled, it is converted into a mixture of two isomeric hydrochlorides, $C_{10}H_{16}.HCl$, one of which is solid and the other liquid. By dissolving them in hot alcohol, the solid compound may be crystallised out in white prisms resembling camphor in appearance and odour. It is termed *artificial camphor* or *dadyl hydrochloride*; it fuses at 115° C. (camphor fuses at 175°) and sublimes on further heating. When its vapour is passed over heated lime, the HCl is removed, and *camphilene* or *dadyl* is obtained, which is isomeric with turpentine, but is optically inactive, and boils at 134° C.

The liquid hydrochloride when distilled with lime yields another optically inactive isomeride called *peucyl* or *terebilene.*

Both terebenthene and australene yield the crystalline hydrochloride, and when these are heated with alkaline salts of weak acids, they yield *camphenes*, which are solid bodies, isomeric with turpentine, fusing at 45° C. and boiling at 160°. They differ, however, in their action on polarised light, that from terebenthene being lævorotatory, and that from australene dextrorotatory.

If an alcoholic solution of turpentine be saturated with HCl gas, crystals are deposited, containing $C_{10}H_{16}.2HCl$. When these are boiled for some time with water, they yield *terpinol*, $(C_{10}H_{16})_2H_2O$, which smells like the hyacinth, and boils at 168° C.

When turpentine is long kept in contact with water, prismatic crystals of *turpentine hydrate* or *terpin*, $C_{10}H_{16}.3H_2O$, are deposited. This body is more quickly prepared by mixing turpentine with one-fourth by measure of dilute nitric acid and one-eighth of alcohol, and exposing to sunshine, with frequent agitation. Terpin dissolves in boiling water, and crystallises on cooling. It fuses at 100° C. and becomes $C_{10}H_{16}.2H_2O$, which sublimes in needle-like crystals at 150° C., and regains the H_2O when exposed to air. When distilled with sulphuric acid, it yields terpinol.

By exposure to air, turpentine is slowly solidified, absorbing oxygen, and forming resinous bodies. Among these is a small quantity of *camphoric peroxide*, $C_{10}H_{14}O_4$, which is decomposed by water, yielding *camphoric acid* and hydric peroxide; $C_{10}H_{14}O_4 + 2H_2O = C_{10}H_{16}O_4 + H_2O_2$. This explains the observation that old oil of turpentine exhibits many of the reactions of hydric peroxide. By passing air and steam through oil of turpentine, a powerfully oxidising solution containing hydric peroxide is obtained, and is employed for disinfecting purposes under the name of *Sanitas*. It is worthy of remark that the leaves of the *Eucalyptus globulus* (gum-tree of Australia), so much esteemed for its sanitary influence, yield an oil similar to oil of turpentine, which becomes brown and resinous when exposed to air.

Terebene, the optically inactive isomeride of turpentine, may be artificially obtained from the fourth olefin, amylene, C_5H_{10}, by polymerising it with sulphuric acid to form *di-amylene*, $C_{10}H_{20}$, converting this into $C_{10}H_{20}Br_2$, and distilling this with alcoholic solution of potash, to abstract $2HBr$ and obtain another olefin, *rutylene*, $C_{10}H_{18}$. If this be converted into $C_{10}H_{18}Br_2$, and distilled with alcoholic potash, it yields terebene, $C_{10}H_{16}$.

333. Oil of turpentine is the representative of a large class of hydrocarbons called the *terpenes*, derived like itself from the vegetable kingdom. All the members of this group contain the same proportions of carbon and hydrogen, and the greater number have the same molecular formula as turpentine, $C_{10}H_{16}$. The terpenes resemble turpentine in their liability to suffer conversion into isomerides, in their solidification by absorption of oxygen when exposed to air, in their combination with water to form crystalline hydrates, and, above all, in their tendency to combine with hydrochloric acid to form crystalline compounds.

The oils of *bergamotte*, *birch*, *chamomile*, *caraway*, *hops*, *juniper*, *lemons*,* *myrtle*, *nutmeg*, *orange*, *parsley*, *pepper*, *savin*, *thyme*, *tolu*, and *valerian* are all terpenes of the formula $C_{10}H_{16}$, and are generally accompanied in the natural oil by the product of its oxidation, bearing a relation to the hydrocarbon similar to that which colophony, $C_{20}H_{30}O_2$, bears to turpentine. Essential *oil of poplar* is a *di-terpene*, $C_{20}H_{32}$.

The oils of *calamus*, *cascarilla*, *cloves*, *cubebs*, *patchouli*, and *rosewood* have the formula $C_{15}H_{24}$.

The essential oils are generally extracted from the flowers, fruit, leaves, or seeds, by distillation with water, the portion of the plant selected being suspended in the still by means of a bag or cage, to prevent it from being scorched by contact with the hot sides of the still, and so contaminating the distillate with *empyreumatic* matters. The water which distils over always holds a little of the essential oil in solution, and it is in this way that the fragrant distilled waters of the druggist are obtained. When the essential oil is present in large proportion, it collects as a separate layer on the surface of the water, from which it is easily decanted. The oil which is dissolved in the water may be separated from it by saturating the liquid with common salt, when the oil rises to the surface; or by shaking it with ether, which dissolves the oil and separates from the water, the ethereal solution floating on the surface, and leaving the oil when the ether is distilled off.

In cases like that of jasmine, where the delicate perfume of the flower would be injured by a high temperature, the flowers are pressed between woollen cloths saturated with oil of poppy-seeds, which thus acquires a powerful odour of the flower. Carbon disulphide is also sometimes employed as a solvent for extracting the essential oils.

Oil of peppermint contains *menthene*, $C_{10}H_{18}$ (and *menthole*, $C_{10}H_{20}O$); essence of cedar wood contains *cedrene*, $C_{16}H_{26}$.

334. *Camphors.*—Closely allied to the essential oils are the different varieties of camphor, which appear to be formed by the oxidation of hydrocarbons corresponding to the essential oils.

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* Oil of lemons and other oils derived from various species of *Citrus* boil at about 176° C., and are termed *citrenes*.

Common camphor ($C_{10}H_{16}O$) is found deposited in minute crystals in the wood of the *Laurus camphora*, or camphor laurel, from which it is obtained by chopping up the branches and distilling them with water in a still, the head of which is filled with straw, upon which the camphor condenses. It is purified by subliming it in large glass vessels containing a little lime.

Camphor passes into vapour easily at the ordinary temperature of the air, and is deposited in brilliant octahedral crystals upon the sides of the bottles in which it is preserved. It fuses at 347° F. (175° C.), and boils at 399° F. (204° C.), and is very inflammable, burning with a bright smoky flame. It is sometimes dissolved in the oil used for the lamps of magic-lanterns, to increase its illuminating power. Camphor is lighter than water (sp. gr. 0.996), and whirls about upon its surface in a remarkable way, dissolving meanwhile very sparingly (1 part in 1000), alcohol and ether being its appropriate solvents.

When distilled with phosphoric anhydride, camphor loses a molecule of water, and yields the hydrocarbon cymene ($C_{10}H_{14}$) homologous with benzene. Cymene is found in the oil of wild thyme.

Borneo camphor ($C_{10}H_{18}O$) is obtained from the exudation of the *Dryobalanops camphora*.* When this exudation is distilled, a hydrocarbon called *bornéène* ($C_{10}H_{16}$), isomeric with oil of turpentine, first passes over, and afterwards the camphor, which is neither so fusible nor so volatile as ordinary camphor, and emits quite a different odour; it also crystallises in prisms instead of octahedra, and may be converted into ordinary camphor by the action of nitric acid, which oxidises 2 atoms of hydrogen, $C_{10}H_{18}O$ (*Borneo camphor*) $- H_2 = C_{10}H_{16}O$ (*Common camphor*).

The Borneo camphor appears to have been formed by the combination of bornéène with water, for if this hydrocarbon be distilled with solution of potash, it combines with a molecule of water, and is converted into the camphor. On the other hand, when Borneo camphor is distilled with phosphoric anhydride, it loses a molecule of water, and yields bornéène. It is interesting to remark that this hydrocarbon is also found in the essential oil of valerian.

The *oil of camphor*, which accompanies the camphor distilled from the camphor laurel, contains an atom of oxygen less than common camphor, its formula being $(C_{10}H_{16})_2O$.

335. *Balsams.*—The vegetable exudations known as balsams are mixtures of essential oils with resins and acids probably produced by the oxidation of the oils.

Balsam of Peru contains an oily substance termed *cinnaméin* ($C_{27}H_{26}O_4$), a crystalline body, *styracin* (C_9H_8O), a crystalline volatile acid, the *cinnamic* ($C_9H_8O_2$), and a peculiar resin.

Balsam of Tolu also contains cinnamic acid and styracin, together with certain resins, which appear to have been formed by the oxidation of styracin.

Storax, also a balsamic exudation, contains the same substances, accompanied by *cinnamene*.

336. *Resins.*—Colophony is the best-known member of the class of resins, which are generally distinguished by their *resinous* appearance, fusibility, inflammability, burning with a smoky flame, insolubility in water, and solubility in alcohol.

As to their chemical composition, they are all rich in carbon and hydrogen, containing generally a small proportion of oxygen, and appear to have been formed, like colophony, by the oxidation of a hydrocarbon analogous to turpentine.

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* The fragrant *essence of lign-aloes* has the same composition as Borneo camphor.

Most of the resins also resemble colophony in their acid characters, their alcoholic solutions reddening blue litmus-paper, and the resins themselves being soluble in the alkalies. This is the case with *sandarach* and *guaiacum resin*, the former of which contains three, and the latter two, resinous acids.

Copal appears to contain several resins, some neutral and some acid, and is distinguished by its difficult solubility in alcohol, in which it can be dissolved only after long exposure to the vapour of the solvent; but if it be exposed to the air for some time, at a moderately high temperature, it absorbs oxygen, and becomes far more easily soluble. Copal is readily dissolved by acetone. *Animi* and *elemi* resins are somewhat similar in properties to copal. All these resins are used in the manufacture of varnishes.

Guaiacum resin is distinguished by its tendency to become blue under the influence of the more refrangible and chemically active (violet) rays of the solar spectrum, as well as under that of certain oxidising agents, such as chlorine and ozone.

Amber, a fossil resinous substance, more nearly resembles this class of bodies than any other, and contains several resinous bodies. It is distinguished by its insolubility, for alcohol dissolves only about one-eighth, and ether about one-tenth, of it. After fusion, however, it becomes soluble in alcohol, and is used in this state for the preparation of varnishes.

Varnishes are prepared by dissolving resins in alcohol, or wood-spirit, or acetone, a little turpentine or some fixed oil being added to prevent the resin from cracking when the solvent has evaporated. In order to promote the solution of the resin, it is usually powdered before being treated with the solvent, and mixed with coarsely powdered glass to prevent it from becoming lumpy.

337. *Caoutchouc*, or india-rubber, may be classed among the hydrocarbons, its chief constituent having the empirical formula C_4H_7. It is procured from a milky exudation furnished by several tropical plants, particularly by the *Hævæa guianensis* and *Jatropha* or *Siphonia elastica*. Incisions are made in these trees, and the milky liquid thus obtained is spread upon a clay bottle-shaped mould, which is then suspended over a fire; a layer of caoutchouc is thus deposited, and its thickness is afterwards increased by repeated applications of the milky liquid, the mould being eventually broken out of the caoutchouc bottle thus formed. The dark colour of commercial india-rubber is believed to be due to the smoke from the fire over which it is dried, for pure caoutchouc is white, and may be obtained by dissolving india-rubber in chloroform, and precipitating with alcohol; the precipitate forms a gummy mass when dried. Commercial india-rubber contains a small quantity of albumen, derived from the original milky liquid, this being really a solution of albumen holding in suspension about 30 per cent. of caoutchouc, which rises to the surface like cream when the juice is mixed with water and allowed to stand, becoming coherent and elastic when exposed to air. It will be remembered that many of the chief uses of caoutchouc depend upon its physical rather than upon its chemical properties, its lightness (sp. gr. 0.93) and impermeability to water adapting it for waterproof clothing, life-buoys, &c., while its remarkable elasticity gives rise to a still greater variety of applications.

For the manufacture of *waterproof cloth*, caoutchouc is dissolved in rectified turpentine, and the solution is spread, in a viscid state, over the surfaces of two pieces of cloth of the same size, which are then laid face to face and passed between rollers, the pressure of which causes perfect adhesion between the surfaces.

Waterproof felt is made by matting together fibres of cotton impregnated with a solution of caoutchouc in naphtha, and passing the felt between rollers. When kept for a long time, its strength and waterproof qualities are deteriorated, in consequence of the oxidation of the caoutchouc, which is thus converted into a resinous substance resembling shell-lac and easily dissolved by alcohol.

Caoutchouc is slowly dissolved by carbon disulphide, benzene, chloroform, coal-naphtha, petroleum, turpentine, and the fixed oils.

Marine glue is a solution of caoutchouc with a little shell-lac in coal-naphtha.

The alkalies and diluted acids are without action on caoutchouc. When gently warmed, it becomes far more soft, pliable, and extensible; it fuses at about 250° F. (121° C.) to an oily liquid, which becomes viscid on cooling, but will not solidify, and is useful for lubricating stop-cocks. When further heated in air, it burns with a bright smoky flame. Heated in a retort, caoutchouc is decomposed into several hydrocarbons, one of which, *isoprene*, C_5H_8, boils at 37° C., and another, *caoutchene*, $C_{10}H_{16}$, boils at 171° C.; they are good solvents for caoutchouc. Caoutchene forms a crystalline compound with water, $C_{10}H_{16}.H_2O$, which may also be obtained by boiling terpin with very dilute sulphuric acid, and distilling with water.

Vulcanised rubber is produced by incorporating india-rubber with 2 or 3 per cent. of sulphur, which not only greatly increases its elasticity, but prevents it from cohering under pressure, and from adhering to other surfaces unless strongly heated. It also becomes insoluble in turpentine and naphtha. Ordinary vulcanised rubber generally contains more sulphur than is stated above, which causes it to become brittle after a time; for some purposes, such as the manufacture of overshoes, other substances are added beside sulphur, such as lead carbonate and zinc oxide. Stoppers made of vulcanised rubber are now often used instead of corks in making apparatus in the laboratory, being far more easily made air-tight; they may be perforated to receive tubes, with a sharp brass cork-borer moistened with alcohol, a very small hole easily stretching to receive a large tube. Boiling alcohol extracts sulphur from them.

When a sheet of caoutchouc is allowed to remain for some time in fused sulphur at 120° C., it absorbs 12 or 15 per cent. without any material alteration, but if it be heated for a short time to 150° C. it becomes vulcanised; and when still further heated, is converted into the black horny substance called *vulcanite* or *ebonite*, and used for the manufacture of combs, &c., and as an electrical insulator.

Vulcanised caoutchouc is sometimes made by mechanically incorporating the sulphur with india-rubber softened by heat; or by immersing the rubber in a mixture of sulphur with chloride of lime, or in carbon disulphide mixed with 2.5 per cent. of S_2Cl_2. It can also be made by dissolving the sulphur in turpentine, which is afterwards used to dissolve the caoutchouc; when the turpentine has evaporated, a mixture of caoutchouc and sulphur is left, which may be easily moulded into any required shape, and afterwards vulcanised by exposure to high-pressure steam having a temperature of about 140° C.

By treating vulcanised caoutchouc with sodium sulphite, the excess of sulphur above 2 or 3 per cent. may be dissolved out. The whole of the sulphur may be removed, and the caoutchouc devulcanised, by boiling with a 10 per cent. solution of caustic soda.

The chemical constitution of vulcanised rubber is not yet understood; it has been suggested that the sulphur has been substituted for a portion of the hydrogen, but it does not seem improbable that the caoutchouc has combined directly with sulphur.

Caoutchouc is by no means rare in the vegetable world, being found in the milky juices of the poppy (and thence in opium), of the lettuce, and of the *euphorbium* and *asclepia* families.

Gutta-percha (empirical formula C_5H_8), like caoutchouc, is originally a milky exudation from incisions made into the wood of the *Isonandra percha*, a native of the Eastern Archipelago. This juice soon solidifies, when exposed to air, to a brown mass heavier than caoutchouc (sp. gr. 0.98) and differing widely from it by being tough and inelastic when cold, and becoming quite soft and plastic when heated nearly to the boiling point of water. Being impervious to water, it is employed as a waterproof material and for water-pipes, and its want of conducting power for electricity is turned to account in the coating of wires for the electric telegraph.

Gutta-percha is dissolved by those substances which dissolve caoutchouc. It is not affected by diluted acids and alkalies, and is used for keeping hydrofluoric acid. It melts easily, and is afterwards decomposed, yielding products similar to those from caoutchouc.

Commercial gutta-percha contains only about 80 per cent. of the hydrocarbon, which may be dissolved out by boiling with ether; the solution, when evaporated, leaves the hydrocarbon as a white powder fusing at 100° C. The portion insoluble in ether contains two resinous bodies soluble in boiling alcohol, which deposits, on cooling, a white crystalline resin, of the empirical formula $C_{10}H_{16}O$, and retains in solution an amorphous resin, $C_{20}H_{32}O$. The existence of these bodies renders it probable that gutta-percha is $C_{20}H_{32}$, the crystalline resin being $C_{20}H_{32}O_2$. This would make gutta-percha a polymeride of turpentine. Exposure to air gradually converts pure gutta-percha into these resinous bodies unless light is excluded.

338. ALCOHOLS.—The hydrocarbons of the marsh-gas series (C_nH_{2n+2}) are convertible into alcohols by substituting the radical hydroxyl (HO) for one of the atoms of hydrogen: thus, methane, CH_4, yields methyl-alcohol, $CH_3.HO$; ethane, C_2H_6, yields ethyl-alcohol, $C_2H_5.HO$; and so on. Hence the general formula of these alcohols would be $C_nH_{2n+1}.HO$, and they form a series, starting from $CH_3.HO$, and increasing by successive additions of CH_2.

Alcohol, $C_2H_5.HO$, is also termed vinic alcohol, or, when mixed with water, *spirit of wine*. It has been already stated that it can be obtained synthetically by combining C and H to form acetylene, C_2H_2, which may be converted into ethene, C_2H_4, by nascent hydrogen; ethene can be combined with sulphuric acid to form sulphethylic acid, $C_2H_5.HSO_4$, from which alcohol may be made by distillation with water. Or ethene may be combined with hydriodic acid to obtain ethyl iodide, C_2H_5I, which, when distilled with caustic potash, yields alcohol—

$$C_2H_5I + KHO = C_2H_5.HO + KI.$$

Naturally, alcohol is found in some unripe fruits. It occurs in coal-tar, in bone-oil, and in the products of distillation of wood.

Preparation.—Alcohol is usually made by the fermentation of glucose or grape-sugar brought about by *yeast*. For a laboratory experiment, two ounces (or 60 grammes) of brown sugar may be dissolved in a pint (or 500 c.c.) of water in a flask, and about a table-spoonful of brewers' yeast (or of German yeast rubbed up with water) added; in a warm room, fermentation soon begins, as indicated by the froth on the surface, caused by bubbles of CO_2. By closing the flask with a cork furnished with a tube dipping under water, the rate of fermentation may be inferred from the escaping gas. When very little more gas is disengaged (usually after about 24 hours) the flask is fitted with a tube connected with a condenser, and the liquid distilled as long as the distillate smells strongly of alcohol. This distillate is then *rectified*, or submitted to a second distillation in a smaller flask or retort, when the first portion which distils over will be much richer in alcohol. This is placed in a narrow bottle, and dried potassium carbonate, in powder, is added by degrees, with frequent shaking, as long as the liquid dissolves it. On standing, two layers are formed, the lower containing the potassium carbonate dissolved in water, and the upper containing the alcohol with about 10 per cent. of water. This upper layer is transferred to a small flask or retort, and allowed to remain for some hours in contact with powdered quick-lime to remove the water; the alcohol is then distilled off in a water-bath.

The mode of action of the yeast in causing the production of alcohol from sugar is not yet known. Yeast is a vegetable substance (*torula cerevisiæ*) which develops from minute spores or germs carried by the air; when these come in contact with a liquid containing the nutriment necessary for the yeast plant, they multiply into a number of round or oval cells arranged in branching chains, visible under the microscope (fig. 275). It is during this growth of the yeast that the conversion of the sugar into alcohol takes place. The pure yeast spores will not produce alcohol from pure sugar, because it does not contain the substances required to nourish the yeast; but when the spores are introduced into grape-juice, or infusion of malt (*wort*), which contain the necessary albuminous matters and phosphates, &c., they grow and cause the formation of alcohol. The crop of yeast thus raised may be used to ferment fresh portions of sugar, and is the more efficacious because, when it is removed from the surface of the liquid in which it has grown, it is accompanied by some of the nutrient materials. When yeast is added to a solution of cane-sugar ($C_{12}H_{22}O_{11}$) it causes it to become glucose, by combining with the elements of a molecule of water; $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. The bulk of the glucose is then decomposed into alcohol and carbonic acid gas; $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. About 95 per cent. of the glucose undergoes this change, and the remainder is converted into other substances, of which the most important are glycerin, $C_3H_5(OH)_3$, and succinic acid, $C_2H_4(CO_2H)_2$, which are always present in fermented alcoholic liquids. The liquid rises in temperature during fermentation, on account of the development of heat in the formation of carbon dioxide. The specific gravity of the solution decreases as the fermentation proceeds, because solution of alcohol is lighter than solution of sugar. A solution containing more than one-fifth of its weight of sugar is not fermented by yeast, and when the alcohol produced in the fermentation amounts to about one-fifth of the weight of the liquid, the growth of the yeast, and therefore the fermentation, is arrested. No fermented liquor, therefore, can contain more than 20 per cent. of alcohol; port wine, the strongest fermented drink, contains, at most, 17 per cent. The yeast does not grow, and fermentation does not take place, at temperatures below 0° C. (32° F.) or above 35° C. (95° F.). The fermentation is also arrested by strong acids, and by antiseptics such as common salt, kreasote, corrosive sublimate, sulphurous acid, and turpentine.

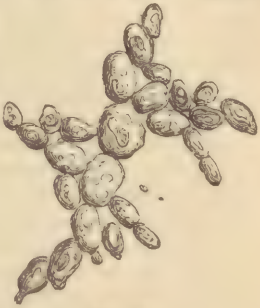

Fig. 275.

In sweat wort (infusion of malt) the yeast increases to six or eight times its original weight.

On the large scale, alcohol is usually made from the starch contained in potatoes, rice, and other grains. The starch, $C_6H_{10}O_5$, is first converted into glucose either by heating it with very diluted sulphuric acid (afterwards neutralised with chalk), or by mixing it with infusion of malt, when

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6,$$

and the glucose is fermented by yeast. The *wash*, as it is termed, is then distilled, the stills being constructed with much ingenuity, to effect the concentration of the alcohol at the least expense.

Even woody fibre, paper, linen, &c., which have the same composition as starch, may be converted into glucose by the action of sulphuric acid, and may thus be made to yield alcohol. New bread, made with yeast, contains about 0.3 per cent. of alcohol, and stale bread about 0.12.

339. *Properties of alcohol.*—Characteristic odour and burning taste; sp. gr. of pure or *absolute* alcohol 0.794 at 15° C. Freezes at $-130°.5$ C.; boiling point 78°.3 C.; takes fire when a flame is brought near its surface, and burns with a pale smokeless flame. Evaporates easily when exposed to the air, without combining with oxygen. Kept in a badly stopped bottle it absorbs water from the air. Alcohol may be mixed with water in all proportions, evolving a little heat, and giving a mixture rather smaller in bulk than the sum of its constituents. This may be shown by filling the vessel, fig. 276, with water up to the neck joining the two globes, carefully filling the upper globe to the brim with (methylated) alcohol, inserting the stopper, and inverting the vessel, when the contraction of the mixture will leave a vacuum in the tube, into which the dissolved air from the water will discharge itself in numerous large bubbles. The greatest contraction occurs when the volumes of alcohol and water are nearly equal (52.3 measures of alcohol to 47.7 of water, or one molecule of alcohol to three molecules of water). The attraction of alcohol for water affords one reason for its power of preserving animal and vegetable substances from putrefaction by removing the water necessary for that change.

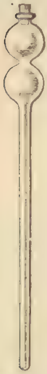
Fig. 276.

Next to water, alcohol is the most valuable simple solvent. It is especially useful for dissolving resins and alkaloids which are insoluble in water. Many salts are capable of combining with alcohol, just as they do with water of crystallisation; examples of such *alcoholates*, as they are termed, are—

$LiCl.4C_2H_6O$ | $MgCl_2.6C_2H_6O$
$CaCl_2.4C_2H_6O$ | $Mg(NO_3)_2.6C_2H_6O$

Ethylates are compounds formed by the replacement of hydrogen in alcohol by metals; they correspond to the hydrates; *e.g.*, sodium ethylate, $C_2H_5.ONa$, aluminium ethylate, $(C_2H_5O)_6Al_2$. Sodium ethylate is used in surgery as a caustic. Water decomposes the ethylates, yielding alcohol and hydrates—

$$C_2H_5ONa + HOH = C_2H_5OH + NaOH.$$

Barium ethylate, $(C_2H_5O)_2Ba$, is obtained by the action of anhydrous baryta on absolute alcohol. A trace of water precipitates barium hydrate from the solution. On heating the alcoholic solution, the barium ethylate precipitates, being less soluble in hot alcohol. The alcoholic solution absorbs carbonic oxide in the cold, yielding a salt isomeric with barium propionate—

$$(C_2H_5O)_2Ba + 2CO = Ba(C_3H_5O_2)_2.$$

Aluminium ethylate, $(C_2H_5O)_6Al_2$, is produced by heating aluminium in alcohol with a little iodine. Probably Al_2I_6 is first produced, which is decomposed by the alcohol, forming aluminium ethylate and hydric iodide; the latter, with the excess of Al, evolves H and forms more Al_2I_6, which decomposes a fresh portion of alcohol, and thus a small quantity of the iodine carries on a continuous action.

Thallium ethylate, $C_2H_5O.Tl$, is a liquid remarkable for its high specific gravity (3.55) and great refractive and dispersive action upon light.

The simplest *chemical test for alcohol* is to add to the suspected liquid hydrochloric acid and enough potassium dichromate to colour it orange-yellow, to divide it between two test-tubes, for comparison, and to heat one of them till the liquid boils; if alcohol be present, the liquid will become green, and evolve the peculiar fragrant smell of aldehyd—

$$2CrO_3 + 6HCl + 3C_2H_6O = Cr_2Cl_6\,(green) + 6H_2O + 3C_2H_4O.$$

A much more delicate test is to gently warm the liquid to be tested, to add a little solid iodine, and then, very carefully, weak potash till the liquid is just bleached. On stirring with a glass rod, a pale yellow crystalline precipitate of *iodoform* is deposited, and its odour, resembling that of saffron, is perceived; $C_2H_6O + 6KHO + I_8 = CHI_3$ (*iodoform*) $+ KCHO_2$ (*potassium formate*) $+ 5KI + 5H_2O$.

Alcohol may also be recognised by the production of acetic acid when its vapour is mixed with air and exposed to the action of platinum-black, which acts by favouring oxidation; $C_2H_6O + O_2 = C_2H_4O_2$ (*acetic acid*) $+ H_2O$. If a small beaker be wetted with alcohol and inverted over a watch-glass containing a few grains of platinum-black, the liquid will soon become acid to litmus.

In contact with air and heated platinum, alcohol yields much aldehyd, as well as acetic acid (see *Lamp without flame*, page 417).

340. The usual method of determining the strength of alcohol is to take its specific gravity by measuring a few cubic centimetres of it into a light stoppered bottle, the weight of which has been ascertained. The weight of the alcohol in grammes will be its specific gravity, very nearly. Rectified spirit has the sp. gr. 0.838, and contains 84 per cent. by weight of alcohol; *proof spirit* (*spiritus tenuior*) has sp. gr. 0.92, and contains only 49 per cent. by weight of alcohol; this is the weakest spirit which will answer to the old rough proof of firing gunpowder which has been moistened with it and kindled. Any spirit weaker than this leaves the powder too wet to explode, and is said to be *below proof*, whilst a stronger spirit is termed *over proof*.

A spirit of 30 per cent., for example, over proof, is one which requires 100 measures of it to be diluted with water to 130 measures in order to reduce it to the strength of proof spirit. A spirit of 30 per cent. below proof contains, in every 100 measures, 70 measures of proof spirit. Some confusion occasionally arises, in commerce, from the practice of calling the percentage of *proof spirit*, in a weak spirit, the percentage of *alcohol*, which amounts to only about half the percentage of proof spirit. Ordinary alcoholic liquids must be distilled before their alcoholic strength can be ascertained by specific gravity, on account of the presence of sugar, colouring matter, &c.

A measured quantity of the liquid is distilled in a flask or retort connected with a good condenser, as long as the distillate contains alcohol; usually one-third of the bulk may be distilled over for wines, and more for spirits. The volume of the distillate is then made equal to that of the liquid before distillation, by adding water, and the specific gravity is determined and compared with a Table of alcoholic strengths. Since the volume of the weak spirit obtained is the same as that of the original liquid, the percentage of alcohol indicated by the Table will be that present in the liquid under examination.

The percentage of alcohol cannot be calculated from the specific gravity, since a given difference does not correspond to a constant quantity of alcohol. Thus, from sp. gr. 1 (water) to 0.9493 (35 per cent. by weight of alcohol) a decrease of 0.0071 in the sp. gr. represents an increase of about 5 per cent. of alcohol, while between sp. gr. 0.9398 (40 per cent. alcohol) and 0.8363 (85 per cent. alcohol) a decrease of .0104 in sp. gr. corresponds to an increase of about 5 per cent. of alcohol.

Suppose the sp. gr. to be 0.9650; then $1 - .9650 = .035$, and $.035 \div .0071 = 4.92$; multiplying this by 5 gives 24.6 for the percentage of alcohol, whilst the exact quantity given in the Tables is 25 per cent. Again, a sp. gr. of .8847 deducted from .9398 (40 per cent. alcohol) gives .0551; dividing this by .0104 and multiplying by 5 we get 26.5, which, added to 40, gives 66.5 per cent. alcohol, the Tables giving 65.

Rule for calculating the approximate percentage of alcohol from its specific gravity.—If above .9493, multiply the difference between the sp. gr. and 1 by 704. If below .9398, subtract the sp. gr. from this, multiply by 480, and add 40.

The weakest fermented alcoholic liquor is *porter*, which contains about 4 per cent. by weight of alcohol; the strongest is *port*, which contains about 17 per cent. Distilled spirits vary greatly in strength, 50 per cent. of alcohol being about the average, though some samples contain 70 per cent.

Methylated spirit is a mixture of 90 parts by weight of rectified spirit with 10 parts of purified wood-spirit added to it by the Excise in order to prevent its use for drinking. It may be distinguished by its odour, and by becoming red-brown with strong sulphuric acid.

When vapour of alcohol is passed through a red-hot tube, it is decomposed into a large number of products, among which are naphthalene, benzene, phenol, aldehyd, acetic acid, acetylene, ethene, marsh gas, carbonic oxide, and hydrogen. A mixture of one molecular weight of alcohol (46) and four molecular weights of water (72) crystallises at − 34° C. When a weak spirit is cooled, ice separates out until the compound $C_2H_6O.4H_2O$ is left as the unfrozen liquid, and when the temperature reaches − 34° it remains constant till the whole has solidified.

341. Alcohol is the most important member of the class of *monohydric alcohols* derived from the hydrocarbons of the paraffin series by the substitution of hydroxyl (HO) for one atom of hydrogen. Like these hydrocarbons, therefore, they form an homologous series, increasing by additions of CH_2. The principal members at present known are shown in the following table:—

Monohydric alcohols, $C_nH_{n2+1}.HO$.

Chemical Name.	Source.	Formula.	Common Name.
1. Methyl-alcohol	Distillation of wood .	$CH_3.HO$	Wood-naphtha
2. Ethyl ,,	Fermentation of sugar .	$C_2H_5.HO$	Spirit of wine
3. Propyl ,,	,, grapes .	$C_3H_7.HO$	
4. Butyl ,,	,, beet .	$C_4H_9.HO$	
5. Amyl ,,	,, potatoes .	$C_5H_{11}.HO$	Fousel oil
6. Caproic ,,	,, grapes .	$C_6H_{13}.HO$	
7. Œnanthic ,,	Distillation of castor-oil with potash . .	$C_7H_{15}.HO$	
8. Caprylic ,,	Essential oil of hog-weed .	$C_8H_{17}.HO$	
9. Nonylic ,,	Nonane from petroleum .	$C_9H_{19}.HO$	
10. Rutic ,,	Oil of rue	$C_{10}H_{21}.HO$	
16. Cetylic ,,	Spermaceti . . .	$C_{16}H_{33}.HO$	Ethal
27. Cerylic ,,	Chinese wax . . .	$C_{27}H_{55}.HO$	Cerotine
30. Melissic ,,	Bees' wax . . .	$C_{30}H_{61}.HO$	Melissine

The great chemical feature of this series is that each alcohol is capable, when oxidised, of yielding an aldehyd, by the removal of H_2 in the form of H_2O, and an acid by the substitution of HO (hydroxyl) for H in the aldehyd; thus, ethyl-alcohol, $CH_3.CH_2.HO$; aldehyd, $CH_3.COH$; acetic acid, $CH_3.CO.OH$.

Moreover, each of these alcohols permits the H in the HO to be replaced by an alcohol-radical, to form an *ether;* thus, ethyl-alcohol, $C_2H_5.HO$, yields common ether, $C_2H_5.O.C_2H_5$.

The usual gradation in properties attending gradation in composition among the members of homologous series is strikingly exemplified in the alcohols. The first seven members of the series are liquid at the ordinary temperature, possess peculiar and powerful odours, and may be easily distilled unchanged. Methylic and ethylic alcohols mix in all proportions with water, but the third member, propylic alcohol, though freely soluble in water, is not so to an unlimited extent, while butylic alcohol is less soluble, and amylic alcohol is very sparingly soluble, in water. Caproic alcohol, the next member, is insoluble in water, while caprylic is not only insoluble, but possesses an oily character, leaving a greasy stain upon paper. The three last members of the series are solids of a wax-like character.

Those members of the series of alcohols which may be distilled without decomposing show a nearly regular increase in the boiling point for each addition of CH_2 in the formula, as shown in the following table:—

Boiling points of the monohydric alcohols.

		Boiling Point C.	Increase.
		°	°
Methyl-alcohol,	CH_4O	60.0	...
Ethyl ,,	C_2H_6O	78.5	18.5
Propyl ,,	C_3H_8O	97.5	19.0
Butyl ,,	$C_4H_{10}O$	117.0	19.5
Amyl ,,	$C_5H_{12}O$	137.0	20.0
Caproyl ,,	$C_6H_{14}O$	157.0	20.0

This gives an average difference of 19°.4 C. for each CH_2 added.

342. *Methyl-alcohol*, or *carbinol*, $CH_3.OH$, is met with, in a very impure state, as *wood-spirit*, or *pyroxylic spirit*, or *pyroligneous ether*, or *wood-naphtha*. When wood is distilled, the condensed products separate into two layers, the lower of which is *wood-tar*, and the upper is a mixture of water with methyl-alcohol, pyroligneous or acetic acid, $CH_3.CO_2H$, acetone, $CH_3.CO.CH_3$, methyl-acetate, $CH_3CO.OCH_3$, &c. On distilling this upper layer, the portion collected below 100° C. contains these bodies; on adding chalk and re-distilling, the acetic acid is retained in the still as calcium acetate, and the distillate is sold as wood-naphtha. Its yellow colour is probably due to *pyroxanthin*, and the milkiness produced by adding water is due to certain oily substances which cause its peculiar odour. In order to obtain methyl-alcohol, the wood-naphtha is distilled with quick-lime to remove water, and heated with fragments of fused calcium chloride, which dissolves in the methyl-alcohol to form a crystalline compound, $CaCl_2(CH_4O)_4$. This mixture is then poured into a retort placed in a water-bath, and heated to 100° C. as long as acetone and methyl acetate distil over. An equal weight of water is then added, which decomposes the compound with $CaCl_2$, and, on continuing the distillation, methylic alcohol passes over accompanied by some water, which may be removed by contact with quick-lime and distilling.

Methyl-alcohol is more easily obtained pure by boiling the wood-naphtha with anhydrous oxalic acid in a flask with a long condensing-tube, or a reversed condenser, until the methyl-alcohol is converted into *methyl oxalate*, $(CH_3)_2C_2O_4$, which separates in crystals on cooling. The crystals are collected on a filter, washed with water, and distilled with solution of potash; $(CH_3)_2C_2O_4 + 2KHO = K_2C_2O_4 + 2(CH_3.HO)$. The methyl-alcohol distils over with some water, which may be removed by quick-lime.

Much methyl-alcohol is now obtained by distilling the refuse of the beet-root sugar manufactory, and has become important as the source of many methyl-compounds employed in making dyes.

Methyl-alcohol in an impure state is used as a solvent for resins in making varnishes.

Properties of methyl-alcohol.—Much resembling ethyl-alcohol, with a somewhat different odour; sp. gr. 0.7997 at 16° C., boiling at 60° C.; very inflammable, burning with a pale flame. Behaves like alcohol to the chromic and iodoform tests; but, in the presence of air and platinum-black, yields (formic aldehyd, $HCOH$, and) formic acid, $CH_3.OH + O_2 = HCO_2H + H_2O$. The formic acid may be distinguished from acetic by its property of reducing silver ammonio-nitrate to the metallic state when warmed with it. Hence, methyl- and ethyl-alcohols may be distinguished by distilling them with dilute sulphuric acid and potassium dichromate, when the former yields formic and the latter acetic acid.

343. *Propyl-alcohol*, or *ethyl-carbinol*, $C_3H_7.OH$, or $CH_2.C_2H_5.OH$, is found in the latter portions of the distillate obtained in rectifying crude spirit of wine. It smells like alcohol, has the sp. gr. 0.82, and boils at 97°.5 C. When mixed with water it may be separated by saturating with calcium chloride, when the propyl-alcohol rises to the surface, which would not be the case with ethyl-alcohol. When oxidised, it yields propyl-aldehyd, $C_2H_5.COH$, and propylic acid, $C_2H_5.CO_2H$.

The *butyl-alcohol*, $C_4H_9.OH$, originally so called, and mentioned in the table at p. 490, as obtained by the fermentation of beet-root, and also by the distillation of crude spirits, is now called *fermentation butyl-alcohol*, or *isobutylic alcohol*, to distinguish it from the *normal butylic alcohol*, which is the real member of this homologous series of alcohols. The two alcohols contain the same proportions of C, H, and O, but the fermentation butyl-alcohol boils at 106° C., and therefore cannot be the normal member of this series, which requires an average increase of 19°.4 C. in the boiling point for each additional carbon atom (see p. 491). Since propyl-alcohol boils at 97°.5, the normal butyl-alcohol should boil at or about 116°.9. Of the difference between these alcohols, and the theoretical explanation of it, more will be said hereafter.

The fermentation butyl-alcohol, $C_4H_9.OH$, or *isopropyl-carbinol*, $CH_2.C_3H_7.OH$, has the smell of fousel oil, which often contains it. It has sp. gr. 0.805, and is much less soluble in water than propyl-alcohol, requiring ten times its weight to dissolve it. Most salts soluble in water cause it to separate on the surface of the liquid.

Normal butyl-alcohol, $C_4H_9.OH$, or *propyl-carbinol*, $CH_2.C_3H_7.OH$, has sp. gr. 0.824, and boils at 117° C. It is obtained by acting upon butyl-aldehyd with water and sodium amalgam to furnish nascent hydrogen—

$$C_3H_7.COH\ (\textit{butyl-aldehyd}) + H_2 = CH_2.C_3H_7.OH\ (\textit{butyl-alcohol}).$$

344. The history of amyl-alcohol resembles that of butyl-alcohol, the name having been originally given to the well-known offensive and poisonous liquid known as *fousel oil*, obtained in the distillation of spirits from fermented grain or potatoes. This contains, however, in addition to fermentation butyl-alcohol, at least two isomeric alcohols, boiling respectively at 128° and 131°, while the normal amyl-alcohol belonging to this series boils at 137°. Fousel oil has the sp. gr. 0.83, and is so sparingly soluble in water that it separates from its solution in distilled spirits on dilution with water, rendering the liquid turbid. Its odour is very characteristic, and the vapour occasions coughing and a sensation of swelling of the head.

Normal amyl-alcohol, $C_5H_{11}.OH$, or *butyl-carbinol*, $CH_2.C_4H_9.OH$, is obtained by the hydrogenation of valeric aldehyd, $C_4H_9.COH$. Its smell resembles that of fousel oil, and its sp. gr. is nearly the same, but it boils at 137° C. When oxidised, it yields valeric aldehyd and valeric acid, $C_4H_9.CO_2H$.

345. *Normal hexylic alcohol*, $C_6H_{13}.OH$, or *amyl-carbinol*, $CH_2.C_5H_{11}.OH$, boiling at 157° C., is not that obtained by fermentation, but is obtained from the essential oil of an umbelliferous plant, *Heracleum giganteum*, which contains *hexylic butyrate*, and yields the alcohol when distilled with potash—

$$C_6H_{13}.C_4H_7O_2 + KHO = C_6H_{13}.OH + KC_4H_7O_2\ (\textit{potassium butyrate}).$$

The *fermentation hexylic alcohol*, or *caproic alcohol*, is that obtained by distilling fermented grape-husks; it has a more unpleasant smell than the normal alcohol, and boils at 149° C.

Œnanthic alcohol, $C_7H_{15}.OH$, or *hexyl-carbinol*, $CH_2.C_6H_{13}.OH$, is obtained by distilling castor oil with potash; it boils above 170° C. The *fermentation œnanthic alcohol*, isomeric with it, and found in the distillate from fermented grape-husks, boils at 165° C.

Caprylic or *octylic alcohol*, $C_8H_{17}.OH$, or *heptyl-carbinol*, $CH_2.C_7H_{15}.OH$, is obtained from the essential oil of the cow-parsnip or hog-weed (*Heracleum sphondylium*), an umbelliferous plant, by distilling it with potash, which decomposes the *octyl acetate*, of which the oil chiefly consists—

$$C_8H_{17}.C_2H_3O_2 + KHO = C_8H_{17}.OH + KC_2H_3O_2\ (\textit{potassium acetate}).$$

It has the sp. gr. 0.83, and boils at 191° C.

Nonylic, $C_9H_{19}.OH$, and *rutic* or *decatylic alcohols*, $C_{10}H_{21}.OH$, are very imperfectly known, and those containing 11, 12, 13, 14, and 15 atoms of carbon have not been prepared.

Cetyl-alcohol, $C_{16}H_{33}.OH$, or *ethal*, is obtained from spermaceti, found in the brain of the sperm-whale. This substance is *cetin* or *cetyl palmitate*, and, when boiled for some time with potash dissolved in alcohol, it yields cetyl-alcohol and potassium palmitate; $C_{16}H_{33}.C_{16}H_{31}O_2 + KHO = C_{16}H_{33}.OH + KC_{16}H_{31}O_2$. On mixing the alcoholic solution with water, the cetyl-alcohol is precipitated in the solid state, being insoluble in water. Cetyl-alcohol is a crystalline body, fusing at 49°.5 C., and boiling at 400°, distilling with partial decomposition.

Ceryl-alcohol, or *cerotin*, $C_{27}H_{55}.OH$, is prepared from *Chinese wax*, the produce of an insect of the cochineal tribe. It consists chiefly of *ceryl cerotate*, and when fused with potash, gives ceryl-alcohol and potassium cerotate—

$$C_{27}H_{55}.C_{27}H_{53}O_2 \ + \ KHO \ = \ C_{27}H_{55}.OH \ + \ KC_{27}H_{53}O_2.$$

By treating the fused mass with water, the cerotate is dissolved, and the ceryl-alcohol is left, and may be obtained in crystals by dissolving it in ether. Its fusing point is 79° C.

Melissyl-alcohol, or *melissine*, $C_{30}H_{61}.OH$, is derived from *bees'-wax*. When this is boiled with alcohol, about one-third of its weight is left undissolved; this is *myricin* or *melissyl palmitate*, $C_{30}H_{61}.C_{16}H_{31}O_2$. By fusing this with potash, it is made to yield potassium palmitate and melissyl-alcohol, which is a crystalline substance, fusing at 88° C.

345*a*. MERCAPTANS, or *thio-alcohols*, or *sulphur alcohols*, are derived from the alcohols by the substitution of sulphur for hydrogen.

Mercaptan, $C_2H_5.SH$, was named from its remarkable action on mercury-compounds (*mercurio aptum*). It is prepared by distilling calcium sulphethylate with potassium hydrosulphide—

$$\underset{\textit{Calcium sulphethylate.}}{Ca(C_2H_5SO_4)_2} \ + \ 2KSH \ = \ CaSO_4 \ + \ K_2SO_4 \ + \ \underset{\textit{Mercaptan.}}{2(C_2H_5.SH)}$$

A solution of potassium hydrosulphide is made by passing H_2S to saturation into potash of sp. gr. 1.3, and this is distilled, in a salt-and-water bath, with an equal volume of solution of calcium sulphethylate of sp. gr. 1.3. The mercaptan forms the upper layer of the distillate. Mercaptan is characterised by its powerful smell of garlic. It is a volatile liquid, of sp. gr. 0.835, and boils at 36° C. A drop exposed to the air is frozen to a crystalline mass by its own evaporation. It burns with a blue flame. Mercaptan is sparingly soluble in water, but dissolves in alcohol and ether. It is unaffected by caustic alkalies, but potassium and sodium act upon it as in the case of alcohol, displacing hydrogen and forming *potassium mercaptide*, $C_2H_5.SK$, and *sodium mercaptide*, which are crystalline bodies soluble in water.

Mercuric oxide reacts with mercaptan, evolving much heat, and forming a white crystalline inodorous compound; $HgO + 2(C_2H_5.SH) = H_2O + (C_2H_5S)_2Hg$ (*mercuric mercaptide*). This is insoluble in water, but may be crystallised from alcohol, or from strong HCl. Potash does not decompose it. H_2S converts the mercury into sulphide and reproduces mercaptan. Mercaptides of other metals may be precipitated by metallic salts from an alcoholic solution of mercaptan. They are also called *thio-ethylates*.

By distilling mercuric thio-ethylate, *di-ethyl sulphide* or *thio-ether*, $C_2H_5.S.C_2H_5$, may be obtained; $(C_2H_5S)_2Hg = (C_2H_5)_2S + HgS$. This may also be prepared by distilling potassium sulphethylate with potassium sulphide; $2KC_2H_5SO_4 + K_2S = 2K_2SO_4 + (C_2H_5)_2S$. It resembles mercaptan, but boils at 92° C. Its alcoholic solution gives, with mercuric chloride, a white crystalline precipitate of $(C_2H_5)_2S.HgCl_2$.

Ethyl disulphide, or *di-ethyl disulphide*, $(C_2H_5)_2S_2$, is obtained when potassium disulphide and sulphethylate are distilled. It may also be formed by heating mercaptan to 150° with sulphur; $2(C_2H_5SH) + S_2 = (C_2H_5)_2S_2 + H_2S$, or by decomposing sodium mercaptide with iodine; $2(C_2H_5SNa) + I_2 = 2NaI + (C_2H_5)_2S_2$. It is an alliaceous liquid, boiling at 151° C.

Ethyl oxysulphide, $(C_2H_5)_2OS$, is a syrupy liquid resulting from the action of dilute nitric acid on ethyl sulphide. *Di-ethyl trisulphide*, $(C_2H_5)_2S_3$, is produced by heating the disulphide with sulphur. *Di-ethyl tetrasulphide*, $(C_2H_5)_2S_4$, is the product of the action of di-sulphur dichloride on mercaptan; $S_2Cl_2 + 2(C_2H_5.SH) = (C_2H_5)_2S_4 + 2HCl$. It is a colourless oil, which is converted into an elastic mass of *di-ethyl pentasulphide*, $(C_2H_5)_2S_5$, by heating to 150° C. in contact with sulphur.

Di-ethyl di-oxysulphide, or *ethyl sulphone*, $(C_2H_5)_2SO_2$, is a very stable crystalline body formed when ethyl sulphide is oxidised by strong nitric acid; it fuses at 70° C. and boils at 248° C., but sublimes at 100° C. It is soluble in water and alcohol.

When ethyl sulphide and ethyl iodide are heated together with a little water for some hours in a flask with an inverted condenser, the mixture, on cooling, deposits colourless prisms of *tri-ethyl-sulphine iodide*, $(C_2H_5)_3S.I$, which are soluble in water and alcohol, but insoluble in ether. This compound is remarkable for producing a series of compounds in which the iodine is replaced by other chlorous radicals, giving rise to *tri-ethyl-sulphine salts*, in which the S is quadrivalent; thus, in the iodide, it is attached to four monad radicals, viz., $(C_2H_5)_3$ and I. By decomposing the iodide with silver hydroxide, the *tri-ethyl-sulphine hydroxide*, $(C_2H_5)_3S.OH$, is obtained; it is a deliquescent crystalline body possessing the properties of a powerful caustic alkali.

Xanthic acid, $C_2H_5.O.CS.SH$, is obtained as a potassium salt by saturating alcohol with potassium hydrate and stirring with excess of carbon disulphide; $C_2H_5.OH + CS_2 + KOH = HOH + C_2H_5.O.CS_2K$ (*potassium xanthate*). This salt forms colourless crystals with a faint odour, soluble in water and alcohol, but not in ether. When it is added to dilute HCl cooled in ice, xanthic acid separates as a heavy colourless oily liquid, which is decomposed at 24° C. into alcohol and CS_2. The characteristic reaction of the xanthates is that with cupric sulphate, which gives at first a dark-brown precipitate of *cupric xanthate*, rapidly decomposing into a yellow oil and bright yellow flakes of *cuprous xanthate*, the reaction being apparently $2(C_2H_5O.CS_2)_2Cu = (C_2H_5O.CS_2)_2Cu_2 + 2\,C_2H_5O.CS_2$

Cupric xanthate *Cuprous xanthate.* *Xanthogen persulphide.*

From this reaction the acid was named (*ξανθός, yellow*).

Xanthic acid may be represented as the sulphur analogue of hydroxypropionic or lactic acid, $C_2H_4(OH).CO.OH$. Potassium propionate is formed when CO_2 acts upon potassium ethylate, while the xanthate is formed when CS_2 acts on $C_2H_5.OH$ and KOH, which are equivalent to potassium ethylate and water.

Ethyl-sulphinic acid, $C_2H_5.SO.OH$, is obtained as a zinc salt by the action of sulphur-dioxide on a cooled ethereal solution of zinc ethide; $Zn(C_2H_5)_2 + 2SO_2 = (C_2H_5.SO_2)_2Zn$. The acid itself is a syrupy liquid. It might evidently be regarded as propionic acid, $C_2H_5.CO.OH$, in which the carbon of the carboxyl is replaced by quadrivalent sulphur.

Ethyl-sulphonic acid, $C_2H_5.SO_2.OH$, is produced when ethyl-sulphinic acid is oxidised by nitric acid; similar treatment also produces it from mercaptan, ethyl polysulphides, and ethyl sulphocyanate. To prepare it, ethyl iodide is heated to 140° C. for some time, with a strong solution of sodium sulphite—

$$C_2H_5I + Na_2.O.SO_2 = NaI + C_2H_5SO_2.ONa$$ (*sodium ethyl-sulphonate*).

Ethyl-sulphonic acid is an oily liquid of sp. gr. 1.3, and may be crystallised by cooling. It forms very soluble salts, which are not easily decomposed by heat. It may be regarded as derived from alcohol, $C_2H_5.OH$, by the substitution, for the OH, of the *sulphuric-acid residue*, $SO_2.OH$ (or SO_4H_2 *minus* OH), while ethyl-sulphinic acid contains the *sulphurous-acid residue*, $SO.OH$ (or SO_3H_2 *minus* OH). By treatment with PCl_5, the OH in ethyl-sulphonic acid may be replaced by Cl, giving *ethyl-sulphonic chloride*, $C_2H_5.SO_2Cl$.

Compounds similar to the foregoing have been obtained from the alcohols formed by the other radicals of this series.

346. DIHYDRIC ALCOHOLS, OR GLYCOLS.—The monohydric alcohols may be regarded as formed upon the model of a molecule of water, H_2O, by replacing half the hydrogen by some univalent radical such as ethyl, C_2H_5, derived from a paraffin-hydrocarbon, such as ethane, C_2H_6, by the loss of an atom of H, the detachment of which has left the residue, C_2H_5, with a *one-atom fixing power*. If two atoms of hydrogen be removed from a paraffin-hydrocarbon, like ethane, it would leave a residue of *two-atom fixing power*, like ethene, C_2H_4, and if the place of the absent hydrogen be occupied by two hydroxyl groups (HO), a dihydric alcohol, or glycol, $C_2H_4(HO)_2$, is obtained, which may be regarded as formed upon the model of a double molecule of water, $H_2(HO)_2$, in which H_2 have been replaced by $(C_2H_4)''$.

Glycol, $C_2H_4(OH)_2$, or *ethene-alcohol*, is a much more artificial product than ethyl-alcohol, having been discovered as lately as 1856. It has at present no practical application, but it will be seen that its importance to theoretical chemistry is very great.

Preparation of glycol.—Glycol is prepared by decomposing ethene dibromide with potassium carbonate. Ethene (p. 472) is first converted into *ethene dibromide* by passing it slowly into 50 grammes of bromine under water, well cooled, until the bromine is bleached, or nearly so. The heavy layer of ethene dibromide is shaken with a little weak potash, the upper watery layer drawn off, and 50 grammes of the dibromide are heated with 40 of potassium carbonate and 100 of water, for eighteen hours, in a flask provided with a reversed condenser (fig. 277); when ethene dibromide no longer condenses and runs back, the condenser is placed in its proper position and the contents of the flask distilled. After all the water has passed over, the flask is strongly heated by a large Bunsen burner, when the glycol distils over. The action of potassium carbonate on ethene dibromide is given by the equation $C_2H_4Br_2 + K_2CO_3 + H_2O = C_2H_4(HO)_2 + 2KBr + CO_2$, which exemplifies the tendency of alkaline reagents, in the presence of water, to effect the replacement of halogens by hydroxyl.

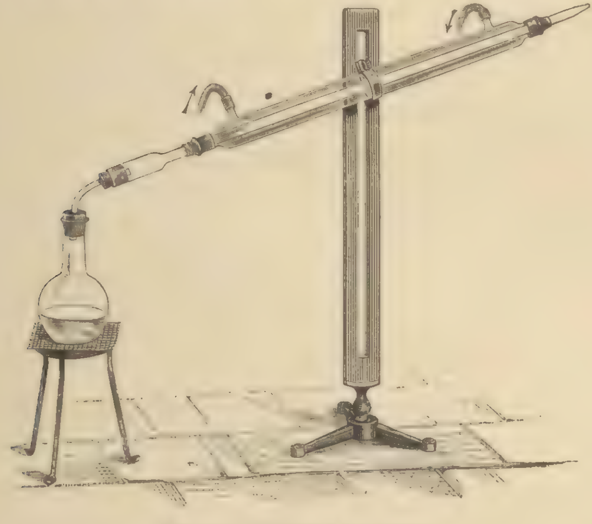

Fig. 277.—Reversed condenser.

Properties of glycol.—A colourless liquid, less mobile than alcohol, and almost inodorous. It has a sweet taste, sp. gr. 1.125 at 0°, and the high boiling point 197° C. Its vapour is inflammable, but will not take fire at common temperatures like alcohol. Glycol mixes with water and alcohol in all proportions, but ether does not dissolve it.

In its chemical characters, glycol bears a general resemblance to alcohol, modified by its dihydric character; thus, sodium dissolves in glycol, as in alcohol, evolving hydrogen, and yielding *monosodium glycol*, or *sodic ethylenate*, $C_2H_4.OH.ONa$, corresponding to sodium ethylate, $C_2H_5.ONa$. On heating this with more sodium, a second atom of H is displaced, yielding *disodium glycol*, or *disodic ethylenate*, $C_2H_4(ONa)_2$. Water converts both compounds into glycol and sodium hydrate.

Glycol chlorhydrin is glycol in which one hydroxyl group has been replaced by Cl : $C_2H_4(HO)Cl$; and is prepared by saturating glycol with HCl, and heating in a sealed tube to 100° C.; $C_2H_4(HO)_2 + HCl = C_2H_4.HO.Cl + HOH$. It has also been obtained by the combination of ethylene, C_2H_4, with hypochlorous acid, HClO. It permits the conversion of a dihydric into a monohydric alcohol, for it yields ethyl-alcohol when acted on by (the nascent hydrogen from) water and sodium-amalgam; $C_2H_4.HO.Cl + 2H = C_2H_5.HO + HCl$.

Under the action of oxidising agents, glycol does not so closely resemble alcohol.

The first product of the oxidation of alcohol is aldehyd, the formation of which is most clearly shown by writing the formulæ thus: alcohol, $CH_3.CH_2OH$; aldehyd, $CH_3.COH$. The first stage in the oxidation of glycol is the formation of *glycol di-aldehyd*, or *glyoxal;* the relation of this body to glycol is shown thus: glycol, $CH_2.OH.CH_2.OH$; glyoxal, COH.COH, or $C_2H_2O_2$. It is formed from glycol, therefore, by the abstraction of H_4, while aldehyd is formed from alcohol by the abstraction of H_2.

When alcohol is further oxidised, it yields acetic acid, $CH_3.CO.OH$, by the conversion of the CH_2 in the alcohol into CO. The further oxidation of glycol yields two acids, *glycolic acid*, $CO.OH.CH_2.OH$, or $C_2H_4O_3$, and *oxalic acid*, CO.OH.CO.OH, or $C_2H_2O_4$.

By heating glycol in a sealed tube with ethylene oxide, *di-ethene tri-alcohol*, $(C_2H_4)''_2H_2O_3$, and *tri-ethene tetralcohol*, $(C_2H_4)''_3H_2O_4$, are produced.

Each member of the olefin series of hydrocarbons has, no doubt, a glycol corresponding to it, but only a few have as yet been examined; these are given in the following table:—

Dihydric alcohols or glycols, $C_nH_{2n}(HO)_2$.

Ethylene-glycol,	$C_2H_4(HO)_2$	Amylene-glycol,	$C_5H_{10}(HO)_2$
Propylene ,,	$C_3H_6(HO)_2$	Hexylene ,,	$C_6H_{12}(HO)_2$
Butylene ,,	$C_4H_8(HO)_2$	Caprylene ,,	$C_8H_{16}(HO)_2$

They are prepared in a similar way to ethylene-glycol, to which they bear a close resemblance. It is remarkable that the glycols containing most carbon have a lower specific gravity than those containing least, while the reverse is observed in other homologous series. Moreover, the boiling points exhibit a similar irregularity. Since the glycols, like the alcohols, form several isomerides, it is not unlikely that the proper distribution into homologous series has not yet been effected.

Only one of the glycols derived from benzene hydrocarbons is known—viz., *xylene glycol*, $C_8H_8(OH)_2$, obtained by passing chlorine into boiling xylene, and decomposing the resulting *tolylene dichloride*, $C_8H_8Cl_2$, with about thirty parts of water at 180° C. The *tolylene dihydrate*, or xylene glycol, crystallises from the aqueous solution in needles, fusing at 112° C. When oxidised by chromic acid, it yields *terephthalic acid*, $C_6H_4(CO.OH)_2$.

347. TRIHYDRIC ALCOHOLS, OR GLYCERINS.—It has been seen that the second member of the paraffin series of hydrocarbons, ethane, C_2H_6, by the loss of H_2, becomes a radical of two-atom fixing power capable of forming a dihydric alcohol; in a similar manner, the third member of the paraffins, propane, C_3H_8, by the loss of H_3, becomes C_3H_5, a radical of three-atom fixing power capable of forming a trihydric alcohol, *glycerin*, $C_3H_5(HO)_3$, which may be represented as formed upon the model of a treble molecule of water, $H_3(HO)_3$, in which H_3 have been replaced by $(C_3H_5)'''$, *propenyl*.

Glycerin, or *glycerol*, or *propenyl-alcohol*, $C_3H_5(OH)_3$, was formerly termed the sweet principle of fats, on account of the facility with which it may be prepared from most of the natural fats, which are thence called *glycerides*. Glycerin is also formed during the alcoholic fermentation of sugar, and is present in small quantity in beer and wine.

Preparation of glycerin.—Palm oil is decomposed in a still by superheated steam, at a temperature of about 315° C., when the condensed liquid in the receiver separates into two layers, the lower of which consists of glycerin dissolved in water; this is evaporated to expel the water, until its sp. gr. reaches 1.15; it is then introduced into a still, and steam of 110° is passed through it as long as the condensed water is acid; it is then distilled over in a current of steam heated to 180°, and condensed in a receiver which is kept too warm to allow the water to condense, so that the glycerin is obtained nearly pure. The chemistry of the process is very simple. Palm oil is *propenyl palmitate*, and is decomposed by water at a high temperature into *propenyl hydrate*, or glycerin, which dissolves in water, and *palmitic acid*, which forms the oily layer above the solution of glycerin in the receiver—

$$\underset{\text{Palmitin.}}{C_3H_5(C_{16}H_{31}O_2)_3} + 3HOH = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Palmitic acid.}}{3HC_{16}H_{31}O_2}.$$

The palmitic acid forms a white crystalline solid on cooling, and is used for making candles.

Glycerin is contained in the refuse liquor of the soap-maker, being always produced when oils and fats are saponified by alkalies, and remaining in solution when the soap is separated by adding salt. As 100 parts of fat, saponified, yield only about 10 parts of glycerin, it does not pay to extract it from the refuse liquors.

Previously to 1850, glycerin was made only on a laboratory scale by the process discovered by Scheele in 1779, which consisted in boiling olive oil with lead oxide (litharge, PbO) and water, when *lead oleate*, or *lead plaster*, remained, while the glycerin dissolved in the water from which it was obtained by evaporation after precipitating the dissolved lead by H_2S.

Glycerin has been made artificially from propene by combining it with chlorine to form *propene dichloride*, $C_3H_6Cl_2$, which is heated with iodine chloride to convert it into *propenyl tri-iodide*, $C_3H_5I_3$; by heating this in a sealed tube, with about twenty times its volume of water, to 160° C., it is converted into glycerin; $C_3H_5I_3 + 3HOH = C_3H_5(OH)_3 + 3HI$.

Properties of glycerin.—Resembles syrup in taste and consistency; sp. gr. 1.269 at 12° C.; boils at 290° C., but then undergoes partial decomposition. It is slightly volatile at 100° C., but not at the ordinary temperature. If kept at 0° C. for some time, a strong aqueous solution of glycerin deposits crystals, especially if a ready-made crystal be introduced; pure glycerin solidifies at $-40°$ C. to a gummy mass. Glycerin does not inflame until it is heated to 150° C., when it burns with a flame resembling that of alcohol. It absorbs water easily from the air, and dissolves without limit in water and alcohol, but is insoluble in ether.

Glycerin is used for sweetening by confectioners and brewers, and, on account of its never drying, it is useful in many cases when it is desired to keep any substance moist and supple. Water mixed with an equal weight of glycerin is sometimes used in gas-meters, being much less easily frozen than water, and less liable to dry up.

It is especially worthy of notice that, under certain conditions, glycerin may be fermented by yeast, when it yields ethyl-alcohol, propyl-alcohol, butyric and caproic acids, and other products; a connecting link is thus established between the alcohols and the sugars.

Glycerin possesses extensive solvent powers, like alcohol, dissolving most substances which are soluble in water, and some others, such as metallic oxides, which are insoluble in water.

Two compounds corresponding to the ethylates may be obtained by the action of sodium ethylate on glycerin dissolved in alcohol, viz., *sodium propenylate*, $C_3H_5(OH)_2ONa$, and *disodium propenylate*, $C_3H_5.OH.(ONa)_2$.

Glycerin does not yield an aldehyd when oxidised, but *glyceric aldehyd*,

$C_2H_3(OH)_2.COH$, has been obtained by electrolysing a mixture of glycerin with dilute sulphuric acid.

When glycerin is carefully oxidised by nitric acid, it yields *glyceric acid*, $C_2H_3(OH)_2.CO.OH$, which is also called *di-hydroxypropionic acid*, since it is propionic acid, $C_2H_5.CO.OH$, in which H_2 have been replaced by $(OH)_2$.

A characteristic property of glycerin is that of yielding an exceedingly pungent and irritating substance, known as *acrolein*, or *acrylic aldehyd*, $C_2H_3.COH$, when sharply heated, or subjected to the action of dehydrating agents, $C_3H_5(OH)_3 = C_2H_3.COH + 2H_2O$. The best test for identifying glycerin is to mix it with powdered $KHSO_4$ and heat it strongly, when the intolerable odour of acrolein is perceived. It is this substance which causes the offensive smell of smouldering candles made of tallow and other glycerides.

Another important property by which glycerin is distinguished is that of conversion into *nitroglycerin*, $C_3H_5(NO_3)_3$, or *propenyl trinitrate*, when cautiously added to a mixture of equal measures of the strongest nitric and sulphuric acids cooled in water. The nitroglycerin separates as a heavy oil when the mixture is poured into much water, and a drop of the oil, placed on an anvil and struck with the hammer, detonates with a deafening report.

The three other glycerins at present known are given below.

Trihydric alcohols, or Glycerols, $C_nH_{2n-1}(HO)_3$.

Propenyl-glycerol,	$C_3H_5(HO)_3$	Pentenyl-glycerol,	$C_5H_9(HO)_3$
Butenyl ,,	$C_4H_7(HO)_3$	Hexenyl ,,	$C_6H_{11}(HO)_3$

348. *Allyl alcohol*, $C_3H_5.OH$, is obtained by heating four parts of glycerin with one part of crystallised oxalic acid, in a retort, to 195° C., as long as water distils over, and afterwards raising the temperature to distil over the allyl alcohol (addition of a little ammonium chloride facilitates the change); the glycerin is first converted into *monoformin*; $C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5(OH)_2.CHO_2 + CO_2 + H_2O$; the monoformin is then decomposed into allyl alcohol, carbon dioxide, and water; $C_3H_5(OH)_2.CHO_2 = C_3H_5.OH + H_2O + CO_2$.

Allyl alcohol has a pungent smell, sp. gr. 0.87, and boils at 96°.6 C. By oxidation it yields *acrylic aldehyd*, or *acrolein*, $C_2H_3.COH$, and *acrylic acid*, $C_2H_3.CO.OH$. Crude wood-spirit contains a little allyl alcohol.

Propargyl or *propinyl alcohol*, $C_3H_3.OH$, is obtained from allyl alcohol by the following steps:—(1) the allyl alcohol is distilled with KBr and H_2SO_4, which gives *allyl bromide*, C_3H_5Br; (2) this is treated with bromine to convert it into *allyl tribromide*, $C_3H_5Br_3$, or *glyceryl tribromide;* (3) when this is distilled with KHO, it yields *dibromoglycid*, $C_3H_4Br_2$, by the loss of HBr; (4) heated with potassium acetate, this gives *bromallyl acetate;* $C_3H_4Br_2 + KC_2H_3O_2 = C_3H_4Br.C_2H_3O_2 + KBr$; (5) when distilled with KHO, bromallyl acetate yields *bromallyl alcohol*, $C_3H_4Br.OH$; (6) bromallyl alcohol is heated with a very strong solution of KHO in a flask with a reversed condenser for some hours; $C_3H_4Br.OH + KHO = C_3H_3.OH + KBr + H_2O$; the mixture is then saturated with CO_2, and distilled, when propargyl alcohol, $C_3H_3.OH$, passes over, dissolved in water, which may be removed by K_2CO_3.

Propargyl alcohol is a fragrant liquid of sp. gr. .96, and boiling point 115° C., burning with a luminous flame. It is distinguished from other alcohols by yielding explosive precipitates with ammoniacal solutions of silver and cuprous salts, in which H is replaced by Ag and Cu′ respectively. A similar reaction, it will be remembered, is exhibited by acetylene, C_2H_2, but this gives a red cuprous compound, while the *cuproso-propargyl alcohol*, $C_3Cu'H_2.OH$, is a green precipitate.

349. *Benzyl alcohol*, or *benzoic alcohol*, $C_7H_7.OH$, may be obtained from *bitter-almond oil* (*benzyl aldehyd*), $C_6H_5.COH$, by heating it with KHO dissolved in alcohol, which oxidises one-half of the aldehyd to potassium benzoate, and fixes the H_2, corresponding to the O, upon the other half of the aldehyd, converting it into the alcohol; $2C_6H_5COH + KOH = C_6H_5.CH_2.OH$ (benzyl alcohol) + $C_6H_5.CO.OK$ (potassium benzoate).

It can also be made from benzoic acid by the action of nascent hydrogen generated by adding sodium amalgam to a boiling solution of the acid; $C_6H_5.CO.OH + H_4 = C_6H_5.CH_2.OH + H_2O$.

The balsams of Tolu and Peru, and storax, yield benzyl alcohol when distilled with alkalies which decompose the benzyl benzoate and cinnamate (*cinnaméin*) contained in them.

Benzyl alcohol is an oily liquid heavier than water (sp. gr. 1.06), boiling at 207° C. Oxidising agents convert it into benzaldehyd (bitter-almond oil) and benzoic acid.

Cinnamyl alcohol, $C_9H_9.OH$, or *styryl alcohol*, or *phenyl-allyl alcohol*, $C_3H_4.C_6H_5.OH$, is also obtained from *storax*, a fragrant balsam exuded by the *Styrax officinale*, a tree found in Syria and Arabia, sometimes used as a pectoral remedy. When this is digested for some hours with a weak solution of soda, and the residue extracted with a mixture of ether and alcohol, needle-like crystals of *styracin* are obtained. This substance is *cinnamyl cinnamate*, $C_9H_9.C_9H_7O_2$, and yields cinnamyl alcohol and potassium cinnamate when distilled with KHO—

$$C_9H_9.C_9H_7O_2 \ + \ KOH \ = \ C_9H_9.OH \ + \ KC_9H_7O_2.$$

Cinnamyl alcohol is a solid body smelling of hyacinths; it crystallises in needles, which fuse at 33° C. and boil at 250°. It dissolves sparingly in water, but easily in alcohol or ether. When oxidised by air, in presence of platinum black, it is converted into *cinnamic aldehyd*, $C_8H_7.COH$, which is the chief constituent of the fragrant oils of cinnamon and cassia. This slowly absorbs more oxygen, and becomes *cinnamic acid*, $C_8H_7.CO.OH$.

Cholesterin, $C_{26}H_{43}.OH$, or *cholesteryl alcohol*, is found in bile and in other animal substances. It is sometimes represented as a homologue of cinnamyl alcohol, for $C_{26}H_{43}.OH = C_9H_9(CH_2)_{17}.OH$, but, as it does not form an aldehyd or an acid, it will not be here described.

350. *Salicyl alcohol*, or *saligenin*, $C_7H_7O.OH$, or *hydroxybenzyl alcohol*, $C_7H_6(HO).OH$, is made from *salicin*, a crystalline substance extracted from willow bark. This substance is a *glucoside*, and when boiled with diluted sulphuric acid it undergoes *hydrolysis*, or decomposition with the elements of water, yielding glucose and salicyl alcohol; $C_{13}H_{18}O_7$ (salicin) + H_2O = $C_6H_{12}O_6$ (glucose) + $C_7H_7O.OH$.

Salicyl alcohol forms tabular crystals, soluble in hot water, in alcohol, and ether, fusing at 82° and subliming at 100°. When oxidised, it yields *salicyl aldehyd*, $C_6H_5O.COH$, or *oil of spiræa*, or *meadow-sweet*, and *salicylic acid*, $C_6H_5O.COOH$.

Saligenin gives an intense blue colour with ferric chloride.

It will be noticed that salicyl aldehyd is metameric with benzoic acid, $C_6H_5.CO.OH$, and that salicylic acid is *hydroxybenzoic acid*, $C_6H_4(HO).CO.OH$.

There are a few substances obtained from plants which are sometimes classed among the alcohols, though they do not yield aldehyds and acids when oxidised, but behave partly as alcohols and partly as sugars (carbohydrates).

Erythrite, *erythro-mannite*, or *phycite*, $C_4H_6(OH)_4$, is often classed as a *tetrahydric alcohol*. It is obtained from certain lichens, such as the *Roccella tinctoria*, or *Orchella weed*, by boiling with milk of lime, filtering, precipitating the excess of lime by CO_2, evaporating the filtrate to a small bulk, and treating with alcohol, when erythrite crystallises out in prisms, which fuse at 120° C. and sublime at 300°, though not quite undecomposed. It is easily soluble in water, and has a sweet taste; sparingly soluble in cold alcohol, and insoluble in ether.

In several of its reactions erythrite resembles glycerin. When it is dissolved in nitric acid, and sulphuric acid added, it yields a crystalline precipitate of *nitro-erythrite*, $C_4H_6(NO_3)_4$, which is explosive like nitroglycerin.

When heated with formic acid, it yields *erythro-glycol*, boiling at about 200° C.; $C_4H_6(OH)_4 + H.CO.OH$ (formic acid) $= C_4H_6(OH)_2$ (erythro-glycol) $+ 2H_2O + CO_2$.

Heated with KHO, erythrite is converted into potassium oxalate and acetate; $C_4H_6(OH)_4 + 3KHO = K_2C_2O_4 + KC_2H_3O_2 + H_2O + 4H_2$.

If, in the treatment of the lichen, cold milk of lime be used, the filtrate, when saturated with CO_2, gives a mixed precipitate of calcium carbonate and *erythrin*, which may be extracted by alcohol, and crystallised. Erythrin is *erythrite di-orsellinate*, $C_4H_6(OH)_2(C_8H_7O_4)_2$, and belongs to the class of ethereal salts. It appears to exist as such in the lichen, and is decomposed into erythrite and calcium orsellinate when boiled with calcium hydrate. Erythrite appears to exist ready formed in certain *algæ*, notably in *Protococcus vulgaris*.

351. *Mannite*, $C_6H_8(OH)_6$, now generally regarded as a *hexhydric alcohol*, is the sweet substance contained in *manna*, from which it may

be extracted by boiling with alcohol, when it crystallises, on cooling, in fine needles fusing at 165° C. It is rather sparingly soluble in cold water and alcohol, but easily on heating, and is insoluble in ether. When oxidised in presence of platinum black, it yields *mannitose*, $C_6H_{12}O_6$, a sugar, isomeric with glucose, which may perhaps be the aldehyd, $C_5H_6(OH)_5.COH$, and when this is further oxidised it becomes *mannitic acid*, $C_5H_6(OH)_5.CO.OH$.

By treatment with nitric acid, mannite is converted into an explosive crystalline body, which is *nitromannite*, or *mannyl hexanitrate*, $C_6H_8(NO_3)_6$.

Mannite is an important substance in vegetable chemistry, since it occurs not only in manna, the dried exudation of the *Ornus*, or manna ash, growing in the South of Europe, but also in the sap of the common ash (*Fraxinus excelsior*), of the larch, apple, cherry, and lime; in the leaves of the syringa and privet; in the bulbs of *Cyclamen europæum* (sow-bread), in the bark of the wild cinnamon, in some lichens, seaweeds, sugar-cane, mushrooms, celery, asparagus, olives, and onions. The seaweed *Laminaria saccharina*, or *sugar-wrack*, contains 12 per cent. of mannite, which is sometimes found as an efflorescence on the surface of the weed. It has also been found in the root of the monkshood (*Aconitum napellus*). The *Agaricus integer*, a common fungus, contains when dry about 20 per cent. of mannite.

Mannite is found among the products of the *viscous fermentation* of saccharine liquors, when they are said to become *ropy;* beet-root juice is especially liable to this change.

Mannite is obtained artificially by the action of nascent hydrogen (sodium-amalgam and water) on grape-sugar; $C_6H_{12}O_6 + H_2 = C_6H_8(OH)_6$; this might lead to the inference that grape-sugar (dextrose) is the aldehyd of mannite.

Mannitane, $C_6H_8(OH)_4O$, is prepared by heating mannite to 200° C.; $C_6H_8(OH)_6 = C_6H_8(OH)_4O + H_2O$. It is a viscous substance very similar to glycerin, and forming compounds when heated with the fatty acids which closely resemble the glycerides, and are saponified by alkalies in the same way. By long exposure to the action of aqueous vapour, it is converted into mannite. The *mannite-glycerides* formed by heating mannite with the fatty acids are ethereal salts of mannitane.

Dulcite, or *melampyrite*, $C_6H_8(OH)_6$, is another hexhydric alcohol, isomeric with mannite, and much resembling it. Dulcite is extracted from Madagascar manna by boiling water. It is nearly twice as soluble in water as mannite, but much less soluble in alcohol. Its fusing point is 182° C., much above that of mannite, from which it also differs in crystalline form.

Dulcite is found in the sap of *Melampyrum nemorosum*, or yellow cow-wheat; also in that of the knotted fig-wort (*Scrophularia nodosa*) and of the common spindle-tree (*Euonymus europæus*). It is artificially prepared from milk-sugar, as mannite is from grape-sugar.

Sorbite, $C_6H_8(OH)_6$, another isomeride of mannite, is found in the berries of the mountain ash (*Sorbus aucuparia*). It is much more fusible than the others, at 110° C.

352. **Aldehyds**, or *dehydrogenated alcohols.*—*Ethyl aldehyd*, or *acetic aldehyd*, $CH_3.COH$, is obtained by distilling alcohol with potassium dichromate and sulphuric acid. The process requires much care, on account of the violence of the action and the volatility of the aldehyd.

Preparation of aldehyd.—Three parts of potassium dichromate, in crystals free from powder, are placed in a flask or retort surrounded by ice (or by a mixture of sodium sulphate crystals with half their weight of HCl), and a mixture of 2 parts ordinary alcohol, 4 parts sulphuric acid, and 12 parts of water, also previously cooled in ice, is added. The flask or retort is then connected with a condenser containing iced water, and the refrigerating mixture removed, when the aldehyd will generally be distilled over by the heat attending the reaction. The impure aldehyd thus obtained is mixed with twice its volume of ether, placed in a bottle surrounded by ice, and saturated with dry ammonia-gas. The ammonia combines with the aldehyd to form a crystalline compound, *aldehyd-ammonia*, $C_2H_4O.NH_3$, which is sparingly soluble in ether; this is drained upon a filter, and distilled with diluted sulphuric acid in a flask or retort, heated by a water-bath, and connected with a condenser filled with iced water. The aldehyd may be freed from water by standing over fused calcium chloride, and distillation.

The preparation of aldehyd illustrates the use of potassium dichromate and sulphuric acid as an oxidising agent upon organic bodies. Neglecting certain secondary reactions, the production of aldehyd may be represented by the equation—

$$3C_2H_5OH + K_2Cr_2O_7 + 4H_2SO_4 = 3CH_3COH + 7H_2O + \underset{\text{Chrome-alum.}}{2KCr(SO_4)_2}$$

On a large scale, aldehyd is obtained as a by-product in the manufacture of alcohol, when it comes over with the first portion of the distillate. Commercial alcohol generally contains a little aldehyd.

Aldehyd may also be obtained by distilling a mixture of an acetate and a formate—

$$\underset{\substack{\text{Potassium}\\\text{acetate.}}}{CH_3.CO.OK} + \underset{\substack{\text{Potassium}\\\text{formate.}}}{H.CO.OK} = \underset{\text{Aldehyd.}}{CH_3.CO.H} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{KO.CO.OK}$$

This illustrates a *general process for obtaining aldehyds*, by distilling the salts of the corresponding acids together with a formate; the calcium salts are best adapted for the purpose.

Properties of aldehyd.—Sp. gr. .80 at 0° C.; boiling point 20°.8 C. Aldehyd has a peculiar acrid odour, which affects the eyes. It mixes in all proportions with water, alcohol, and ether. It has a great disposition to combine with oxygen to form acetic acid; $CH_3.COH + O_2 = CH_3.CO.OH + H_2O$. Hence aldehyd acts as a reducing agent, and one of the tests for it is the reduction of silver nitrate to the metallic state. If a few crystals of aldehyd-ammonia be dissolved in water, a little silver nitrate added, and a gentle heat applied, the silver will be deposited on the sides of the flask or tube, giving them the reflecting power of a mirror.

Another characteristic property of aldehyds is that of forming crystalline compounds with hydrogen sodium sulphite (sodium bisulphite). If aldehyd be mixed with a saturated solution of $NaHSO_3$, it forms a crystalline compound, $C_2H_4O.NaHSO_3$, from which the aldehyd may be obtained by distillation with either acids or alkalies.

When mixed with potash, and gradually heated to boiling, aldehyd yields a brown-yellow substance of peculiar odour, known as *aldehyd-resin*; its chemical constitution is uncertain.

A *general test for aldehyds* is their power of restoring the red colour to a solution of a salt of rosaniline which has been bleached by sulphurous acid.

Nascent hydrogen (water and sodium-amalgam) converts aldehyd into alcohol; $CH_3.COH + H_2 = CH_3.CH_2.OH$ (alcohol).

Perfectly pure aldehyd can be kept unchanged; but in the presence of a very small quantity of hydrochloric or sulphurous acid, or of carbon oxychloride, it undergoes a polymeric transformation into *paraldehyd* (or *elaldehyd*), $C_6H_{12}O_3$, which is much heavier (sp. gr. .998 at 15° C.), and boils at 124° C. It crystallises in prisms at 10° C. Pure aldehyd, to which a drop of strong sulphuric acid is added, evolves heat and diminishes in volume, and when cooled in a freezing mixture deposits crystals of paraldehyd.

Paraldehyd is sparingly soluble in cold water, and even less soluble in hot water. It may be reconverted into aldehyd by distillation with sulphuric or hydrochloric acid, or by strongly heating its vapour. Paraldehyd is sometimes administered to procure sleep.

Another polymeric modification of aldehyd, of unknown molecular weight, is termed *metaldehyd*, and sometimes crystallises in needles from aldehyd when kept. It may be obtained by cooling aldehyd in a freezing-mixture, and passing a few bubbles of HCl or SO_2, when metaldehyd crystallises out. It sublimes at 100° C. without fusing, is insoluble in water, and sparingly soluble in alcohol and ether. When distilled with dilute sulphuric acid, or heated in a sealed tube to 116° C., it is reconverted into aldehyd.

Aldehyd is employed in the manufacture of some of the aniline dyes.

353. Aldehyd is the representative of a class of compounds having many properties in common, which are probably as numerous as the alcohols from which they are derived.

The chief aldehyds at present known are shown in the following table :—

Chemical Name.	Source.	Formula.
Formic aldehyd	Oxidation of methyl-alcohol	$H.COH$
Acetic ,,	,, ethyl ,,	$CH_3.COH$
Propylic ,,	,, propyl ,,	$C_2H_5.COH$
Butyric ,,	,, butyl ,,	$C_3H_7.COH$
Valeric ,,	,, amyl ,,	$C_4H_9.COH$
Caproic ,,	Distillation of calcium formate with calcium caproate	$C_5H_{11}.COH$
Œnanthic ,,	Distillation of castor oil	$C_6H_{13}.COH$
Caprylic ,,	,, ,,	$C_7H_{15}.COH$
Rutic ,,	Oil of rue	$C_9H_{19}.COH$
Euodic ,,	,,	$C_{10}H_{21}.COH$
Lauric ,,	,,	$C_{11}H_{23}.COH$
Myristic ,,		$C_{13}H_{27}.COH$
Palmitic ,,		$C_{15}H_{31}.COH$
Stearic ,,		$C_{17}H_{35}.COH$
Glyoxal	Oxidation of glycol	$COH.COH$
Glyceric ,,		$C_2H_3(OH)_2.COH$
Acrylic ,,	Oxidation of allyl-alcohol	$C_2H_3.COH$
Crotonic ,,		$C_3H_5.COH$
Benzoic ,,	Bitter-almond oil	$C_6H_5.COH$
Cinnamic ,,	Oil of cinnamon	$C_8H_7.COH$
Salicylic ,,	,, meadow-sweet	$C_6H_5O.COH$
Cuminic ,,	,, cumin	$C_9H_{11}.COH$
Anisic ,,	,, anise	$C_7H_7O.COH$
Vanillic ,,	Vanilla pods	$C_7H_7O_2.COH$
Pyromucic ,,	Distillation of bran with dilute sulphuric acid	$C_4H_3O.COH$

354. *Formic aldehyd*, or *methyl aldehyd*, $H.COH$, which is a gas, has not been obtained in a pure state, but a solution of it in methyl-alcohol is prepared by passing a mixture of the alcohol vapour and air over platinum wire heated to redness, and condensing the product; $CH_3.OH + O = H.COH + H_2O$. It reduces silver ammonio-nitrate, like ethyl-aldehyd, being converted into formic acid, $H.CO.OH$. When its solution is evaporated *in vacuo* over sulphuric acid, a part of it becomes converted into a crystalline solid, insoluble in water, alcohol, and ether, known as *paraformaldehyd*, which is polymeric with formic aldehyd, having the formula $C_3H_6O_3$. When heated, it begins to volatilise at 100° C., fuses at 152°, and is converted into formic aldehyd gas; if this be collected over mercury, it becomes gradually reconverted into paraformaldehyd.

Propylic aldehyd, $C_2H_5.COH$, is obtained by distilling a mixture of calcium propylate with calcium formate—

$$(C_2H_5.CO_2)_2Ca + (H.CO_2)_2Ca = 2C_2H_5COH + 2CaCO_3.$$

It resembles aldehyd in odour and specific gravity, but boils at 49° C., and is less miscible with water.

Butyric aldehyd, $C_3H_7.COH$, obtained by a similar process, is sparingly soluble in water, and boils at 75° C.

Acetic, propylic, and butyric aldehyds occur among the products of the oxidising action of a mixture of manganese dioxide with sulphuric acid upon albumen, fibrin, and casein.

Valeric aldehyd, $C_4H_9.COH$, is prepared by distilling calcium formate with calcium valerate; $(C_4H_9.CO_2)_2Ca$. It is also sparingly soluble in water, and boils at about 102° C.

Valeral, isomeric with valeric aldehyd, is prepared from fermentation amyl alcohol, or fousel oil, by distillation with sulphuric acid and potassium dichromate. The acid distillate is neutralised by shaking with potash, and the upper layer of liquid is shaken with a strong solution of hydrogen sodium sulphite, which combines with the valeral, and precipitates it as a crystalline compound from which valeral may be obtained by distillation with caustic soda.

Valeral, or *isovaleric aldehyd*, has a characteristic and oppressive smell of apples. It has sp. gr. 0.82, and boils at 92°.5 C.

Caproic aldehyd, $C_5H_{11}.COH$, obtained from calcium formate and caproate, has sp. gr. 0.84, and boils at 128° C.

Œnanthic aldehyd, or *œnanthol*, $C_6H_{13}.COH$, is extracted by hydrogen sodium sulphite from the liquid obtained by the destructive distillation of castor oil. It has a nauseous odour, sp. gr. 0.827, and boiling point 152° C.

Lauric aldehyd, $C_{11}H_{23}.COH$, contained in oil of rue, is a crystalline solid, without smell, fusing at 45°.

Myristic aldehyd, $C_{13}H_{27}.COH$, is also solid, fusing at 53°.

Palmitic aldehyd, $C_{15}H_{31}.COH$, fuses at 59°.

Stearic aldehyd, $C_{17}H_{35}.COH$, fuses at 64°.

The aldehyds derived from the monohydric alcohols have several isomerides, like the alcohols, and these will be more particularly referred to in discussing the structure of organic compounds.

355. *Glyoxal*, or *oxalic aldehyd*, COH.COH, is prepared by slowly oxidising acetic aldehyd with dilute nitric acid. It occurs among the products of the regulated action of nitric acid on alcohol and glycol.

It is a deliquescent solid, soluble in water, alcohol, and ether, forming a crystalline compound with $NaHSO_3$, and reducing silver nitrate, becoming oxidised to oxalic acid, $CO_2H.CO_2H$, and glyoxalic acid, $CHO.CO_2H$. Potash and soda convert it into a yellow resinous body. With ammonia, it yields *glycosine*—

$$3C_2H_2O_2 + 4NH_3 = 6H_2O + N_4(C_2H_2)_3.$$

Glyoxalic or *glyoxylic acid*, $CHO.CO_2H$, contains the characteristic radicals of the aldehyds (CHO) and the acids (CO_2H), and hence it is an *aldehyd acid* capable of forming salts by the replacement of the H in the acid radical by a metal, and at the same time resembling the aldehyds in its reducing properties, and in forming a crystalline compound with $NaHSO_3$. Oxidation converts it into oxalic acid; $Ag_2O + CHO.CO_2H = Ag_2 + CO_2H.CO_2H$.

Acrolein, or *acrylic aldehyd*, $C_2H_3.COH$, is prepared by distilling glycerin with twice its weight of hydrogen potassium sulphate (bisulphate of potash), which abstracts the elements of two molecules of water; $C_3H_5(OH)_3 = C_2H_3.COH + 2H_2O$. The crude acrolein is shaken with PbO_2 to remove SO_2, and rectified over $CaCl_2$ to remove the water.

Acrolein is distinguished by a very powerful irritating odour. It is a liquid of sp. gr. .84, boiling at 52° C. It dissolves sparingly in water, but easily in alcohol and ether. Unlike most aldehyds, it does not combine with $NaHSO_3$; but it forms a resinous body with potash and soda, and reduces ammoniacal $AgNO_3$, which converts it into acrylic acid, $C_2H_3.CO_2H$. Sodium amalgam and water (nascent hydrogen) convert it into allyl-alcohol, $C_3H_5.OH$. When kept, acrolein becomes a white solid, *disacryl*, which appears to be polymeric with it, but cannot be reconverted. HCl gas passed into acrolein converts it into a crystalline body, $C_3H_4O.HCl$, which, when distilled with potash, yields *metacrolein*, $C_9H_{12}O_3$, corresponding to paraldehyd.

Metacrolein is crystalline, fuses at 50° C., and boils at 170°, being partly converted into acrolein; it is nearly insoluble in water, but soluble in alcohol.

Crotonic aldehyd, $C_3H_5.COH$, is prepared by heating acetic aldehyd to 100° C. for two days in contact with $ZnCl_2$ and a little water—

$$2(CH_3.COH) = H_2O + C_3H_5.COH.$$

The $ZnCl_2$ acts as a dehydrating agent. The unchanged aldehyd is distilled off, some water added, and the distillation continued, when water and croton aldehyd distil over.

Crotonic aldehyd has an irritating odour like acrolein. It boils at 104° C., and is sparingly soluble in water. When oxidised by air or silver oxide, it yields crotonic acid, $C_3H_5.CO_2H$. It occurs in some kinds of fousel oil.

356. *Benzoic aldehyd*, or *bitter-almond oil*, $C_6H_5.COH$, was originally made by distilling the moistened bitter-almond cake, from which the *fixed* oil had been extracted by pressure. The cake was placed in a perforated vessel and subjected to the action of steam, which carried over the oil and deposited it as a heavy layer on standing.

The bitter-almond oil does not exist ready formed in the almond, but is a product of the decomposition of the bitter substance, *amygdalin*, $C_{20}H_{27}NO_{11}$, of which the bitter almond contains about 5 per cent. This substance is a glucoside, and is decomposed, in the presence of water and of a peculiar albuminoid ferment present in the almond and known as *emulsin*, into glucose, bitter-almond oil, and hydrocyanic acid—

$$C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_7H_6O + HCN.$$

The presence of hydrocyanic acid renders the crude oil of bitter almonds poisonous. It may be purified either by re-distilling with lime and ferrous chloride, when the HCN is converted into Prussian blue; or by shaking it with an equal volume of a strong solution of hydrogen sodium sulphite, which combines with the benzoic aldehyd to form a crystalline compound, from which the pure oil may be obtained by distillation with sodium carbonate.

Bitter-almond oil is made artificially from toluene. When chlorine is passed into boiling toluene, *benzylene dichloride* is produced—

$$C_6H_5.CH_3 + Cl_4 = C_6H_5.CHCl_2 + 2HCl.$$

By distilling benzylene dichloride with potash, it is converted into bitter-almond oil—

$$C_6H_5.CHCl_2 + 2KHO = 2KCl + H_2O + C_6H_5.CHO.$$

Boiling with water and lead nitrate is sometimes employed to effect the conversion.

Benzoic aldehyd is a colourless or pale yellow liquid, of characteristic odour, boiling at 180° C., and of sp. gr. 1.05. It is very sparingly soluble in water, but dissolves in alcohol, and is precipitated on addition of water. It is often sold in alcoholic solution. The oxidising action of air gradually converts benzoic aldehyd into crystals of benzoic acid; $C_6H_5.COH + O = C_6H_5.CO_2H$. The presence of hydrocyanic acid retards this conversion. It has less reducing action on metallic salts than is exerted by the aldehyds of the acetic series. Benzoic aldehyd is dissolved by a strong solution of sodium sulphite, and if dilute sulphuric acid be added, drop by drop, to this solution, it presently deposits voluminous crystals of the compound of benzaldehyd with the acid sulphite, $C_7H_6O.NaHSO_3$; the crystals dissolve on heating, and are deposited again on cooling.

In contact with solution of ammonia, benzoic aldehyd is slowly converted into a crystalline mass of *hydrobenzamide*—

$$3(C_6H_5.CHO) + 2NH_3 = (C_6H_5CH)_3N_2 + 3H_2O.$$

This reaction distinguishes the *aromatic aldehyds* from the aldehyds of the acetic series, which simply combine with ammonia (p. 501).

The crude oil of bitter almonds contains a crystalline body termed *benzoine*, $C_{14}H_{12}O_2$, which is polymeric with benzaldehyd, into which it may be converted by passing its vapour through a red-hot tube. Benzoine is also formed by the contact of benzaldehyd with potassium cyanide dissolved in alcohol, so that it is produced when the crude oil containing hydric cyanide is shaken with alcoholic solution of potash, which produces potassium cyanide. When pure benzoic aldehyd is treated with alcoholic solution of potash, it yields benzoic alcohol and benzoic acid (p. 498). A good method of identifying bitter-almond oil is to heat it in a test-tube with a piece of caustic potash, to dissolve the cooled mass in water, and add HCl, which precipitates feathery crystals of benzoic acid; $C_6H_5.COH + KHO = C_6H_5.CO.OK$ (potassium benzoate) $+ H_2$.

When bitter-almond oil is heated with a strong solution of hydriodic acid in a sealed tube, it is converted into toluene; $C_6H_5.COH + 2HI = C_6H_5.CH_3 + H_2O + I_2$.

Cinnamic aldehyd, $C_8H_7.COH$, occurs in the essential oils of cinnamon and cassia, and is very similar in its chemical properties to benzoic aldehyd. When oxidised, it yields *cinnamic acid*, $C_8H_7.CO_2H$, and, with ammonia, it gives *cinnhydramide*, $(C_8H_7.CH)_3N_2$.

Cinnamaldehyd may also be obtained by mixing benzoic and acetic aldehyds, and passing HCl gas, which acts as a dehydrating agent—

$$C_6H_5.COH \ + \ CH_3.COH \ = \ C_8H_7.COH \ + \ H_2O.$$

357. *Salicylic aldehyd*, $C_6H_5O.COH$, or *oil of spiræa* (meadow-sweet), is made by distilling salicin (from willow-bark) with potassium dichromate and sulphuric acid; 10 grms. of potassium dichromate are dissolved in 120 grms. water and mixed with 15 grms. sulphuric acid. When the mixture is cool, it is poured upon 10 grms. of salicin in a retort, set aside for twenty-four hours, and distillation is conducted by a moderate heat; the aldehyd condenses with the water, and forms a layer beneath it. It was pointed out (at p. 499) that salicin, when boiled with dilute sulphuric acid, yields glucose and salicylic alcohol; this is oxidised by the chromic acid and converted into salicylic aldehyd.

Salicylic aldehyd may also be obtained by the action of chloroform and caustic soda on phenol (carbolic acid). Two parts of phenol and 4 parts of sodium hydrate are dissolved in 6 parts of water in a flask or retort furnished with a tap-funnel and an inverted condenser; run in gradually 3 parts of chloroform, shaking after each addition; when the action has ceased, boil for half an hour, allow the liquid to cool, and acidify with dilute sulphuric acid; place the condenser in its proper position, and pass steam through the contents of the retort; the oily layer under the water in the receiver is dissolved in ether and shaken with solution of $NaHSO_3$, which combines with the salicyl aldehyd and leaves the phenol dissolved in the ether, which rises to the surface; draw off the lower aqueous layer and acidulate it with dilute sulphuric acid, which separates the aldehyd as a heavy oil. The action of chloroform and sodium hydrate upon phenol produces sodium salicyl aldehyd—

$$C_6H_5.OH \ + \ 4NaHO \ + \ CHCl_3 \ = \ C_6H_4NaO.COH \ + \ 3NaCl \ + \ 3H_2O.$$

The sodium compound, when decomposed by sulphuric acid, yields the aldehyd; $C_6H_4NaO.COH + H_2SO_4 = C_6H_5O.COH + NaHSO_4$.

Salicyl aldehyd is a colourless fragrant liquid, of sp. gr. 1.17 and boiling point 196° C. It is sparingly soluble in water, but dissolves in alcohol. Its solution gives an intense violet colour with ferric chloride. It resembles benzoic aldehyd in its behaviour with ammonia, which converts it into *hydrosalicylamide*, $(C_6H_5O.CH)_3N_2$; but it differs from benzoic and cinnamic aldehyds by easily combining with alkalies to form compounds in which an atom of hydrogen is displaced by the metal; thus, $C_6H_5O.COH + KHO = C_6H_4KO.COH + H_2O$. This reaction indicates that salicyl aldehyd is *hydroxybenzaldehyd*, $C_6H_4.HO.COH$, and connects this aldehyd with the class of phenols, which it also resembles in its intense coloration with ferric chloride; but the phenols are not oxidisable into corresponding acids nor reducible to alcohols, whereas salicyl aldehyd is oxidised to salicylic acid, $C_6H_5O.CO_2H$, and is converted into salicyl alcohol by nascent hydrogen (water and sodium amalgam). Coumarin, which causes the smell of hay, has been made artificially from salicyl aldehyd by a process to be described hereafter.

The *dihydroxybenzaldehyd*, or *proto-catechuic aldehyd*, $C_6H_3(HO)_2.COH$, is not of any practical importance. It is a crystalline substance soluble in water.

Cuminic or *cumic aldehyd*, or *cuminol*, $C_9H_{11}.COH$, occurs in the aromatic oils of cummin, caraway, and water-hemlock, all umbelliferous plants, and is extracted from the oil by shaking with solution of $NaHSO_3$, which forms a crystalline compound with it. It is liquid, fragrant, and boils at 236° C. Its chemical relations resemble those of benzoic aldehyd. It appears to be *butyl-benzyl aldehyd*, $C_6H_4.C_3H_7.COH$.

Anisic aldehyd, $C_7H_7O.COH$, is prepared by heating the essential oils of anise and fennel (both umbelliferous plants) with dilute nitric acid. These oils contain a fragrant camphor-like substance termed *anethol*, $C_{10}H_{12}O$, which there is some ground for representing as derived from phenol, $C_6H_5.OH$, by the replacement of H in C_6H_5 by allyl, and of the H in OH by methyl, leading to the rational formula $C_6H_4.C_3H_5.OCH_3$. Its conversion into anisic aldehyd by the oxidising action of nitric acid might then be expressed by the equation

$$C_6H_4.C_3H_5.OCH_3 + O_7 = C_6H_4.OCH_3.COH + 2CO_2 + 2H_2O.$$

Anisic aldehyd is a fragrant liquid, boiling at 250° C., and much resembling benzoic aldehyd in its reactions. An alcoholic solution of potash causes its decomposition into anisic alcohol, $C_8H_9O.OH$, and anisic acid, $C_7H_7O.CO_2H$.

Vanillic aldehyd, or *vanillin*, $C_7H_7O_2.COH$, is extracted from the pods of *Vanilla planifolia*, a Mexican orchidaceous plant. Its crystals are visible in these pods, and it may be extracted by boiling them with alcohol. It forms needles fusing at 80° C. and subliming at 150°. It is rather sparingly soluble in water, but soluble in alcohol and ether. Vanillin is characterised by its aromatic taste and odour, and is much used for flavouring. It is now made artificially from *coniferin*, a crystalline glucoside obtained in abundance from coniferous trees (see *Glucosides*). The title of vanillin to rank with the aldehyds is sometimes questioned, for it reacts with bases like an acid; but the reducing action of moist sodium amalgam converts it into *vanillic alcohol*, $C_8H_9O_2.OH$, and oxidation by exposure to air converts it into *vanillic acid*, $C_7H_7O_2.CO_2H$.

358. *Pyromucic aldehyd*, or *furfurol*, or *oil of ants*, $C_4H_3O.COH$, is prepared by distilling the bran of wheat, freed from starch and gluten by steeping in a cold weak solution of potash, with half its weight of sulphuric acid, previously diluted with an equal bulk of water, a current of steam being forced through the mixture; the furfurol distils over with the water, from which it may be separated by adding common salt. A hundred parts of bran yield about 3 of furfurol. It has also been obtained from sawdust by the action of steam at 100 lbs. pressure. Furfurol accompanies the formic acid (hence its old name, oil of ants) obtained by distilling sugar and starch with MnO_2 and H_2SO_4. It is also present in fousel oil from crude spirits. Furfurol is a colourless liquid smelling of bitter almonds, of sp. gr. 1.17 and boiling point 163° C. It dissolves in twelve times its weight of water, and is freely soluble in alcohol. Strong sulphuric acid dissolves it to a purple liquid, from which water precipitates it unchanged. It becomes brown when exposed to the air. Furfurol combines with $NaHSO_3$, and reduces silver. With ammonia it behaves as an aromatic aldehyd, forming *furfuramide*, $(C_4H_3O.CH)_3N_2$, in which three molecules of furfurol have exchanged O''_3 for N'''_2.

By oxidation, furfurol is converted into *pyromucic acid*, $C_4H_3O.CO_2H$. Alcoholic solution of potash converts it into potassium pyromucate and *furfuryl alcohol*, $C_5H_5O.OH$. (Pyromucic acid is obtained by distilling the mucic acid derived from the oxidation of gum or milk-sugar.)

Fucusol is isomeric with furfurol, and is prepared in a similar way, from certain varieties of *fucus* (seaweed).

359. ORGANIC ACIDS.—It will have been observed in the formulæ above given for different acids, that they all contain the group CO_2H, *carboxyl* or *oxatyl*, instead of the group COH, which distinguishes the aldehyds. The characteristic feature of an organic acid is its readiness to permit the replacement of the H in CO_2H by a metal to form a salt. When an acid contains two CO_2H groups, it permits the two hydrogen atoms to be replaced by a metal, and is a *dibasic* acid, or if there are three CO_2H groups, it is a *tribasic* acid, and so on.

The most important organic acids are enumerated in the following tables, arranged, as far as possible, in their proper chemical groups:—

Monobasic acids of the acetic series, $C_nH_{2n+1}CO_2H$.

Acid.	Source.	Formula.
Formic . . .	Red ants, nettles	$H.CO_2H$
Acetic . . .	Vinegar	$CH_3.CO_2H$
Propylic . . .	Oxidation of oils	$C_2H_5.CO_2H$
Butyric . . .	Rancid butter	$C_3H_7.CO_2H$
Valeric . . .	Valerian root	$C_4H_9.CO_2H$

Monobasic acids of the acetic series—(continued).

Acid.	Source.	Formula.
Caproic	Rancid butter	$C_5H_{11}.CO_2H$
Œnanthic	Oxidation of castor oil	$C_6H_{13}.CO_2H$
Caprylic	Rancid butter	$C_7H_{15}.CO_2H$
Pelargonic	Geranium leaves	$C_8H_{17}.CO_2H$
Rutic or Capric	Rancid butter	$C_9H_{19}.CO_2H$
Euodic	Oil of rue	$C_{10}H_{21}.CO_2H$
Lauric	Bay berries	$C_{11}H_{23}.CO_2H$
Cocinic	Cocoa-nut oil	$C_{12}H_{25}.CO_2H$
Myristic	Nutmeg-butter	$C_{13}H_{27}.CO_2H$
Pentadecylic	*Agaricus integer* (a fungus)	$C_{14}H_{29}.CO_2H$
Palmitic	Palm oil	$C_{15}H_{31}.CO_2H$
Margaric		$C_{16}H_{33}.CO_2H$
Stearic	Tallow	$C_{17}H_{35}.CO_2H$
Balenic		$C_{18}H_{37}.CO_2H$
Butic	Butter	$C_{19}H_{39}.CO_2H$
Nardic		$C_{20}H_{41}.CO_2H$
Behenic		$C_{21}H_{43}.CO_2H$
Lignoceric	Beech-wood tar	$C_{23}H_{47}.CO_2H$
Hyænic		$C_{24}H_{49}.CO_2H$
Cerotic	Bees'-wax	$C_{26}H_{53}.CO_2H$
Melissic	,,	$C_{29}H_{59}.CO_2H$

Monobasic acids of the acrylic series, $C_nH_{2n-1}CO_2H$.

Acrylic	Oxidation of acrolein	$C_2H_3.CO_2H$
Crotonic		$C_3H_5.CO_2H$
Angelic	Angelica root	$C_4H_7.CO_2H$
Pyroterebic	Turpentine	$C_5H_9.CO_2H$
Damaluric	Cow's urine	$C_6H_{11}.CO_2H$
Campholic	Camphor	$C_9H_{17}.CO_2H$
Cimicic	Tree-bug	$C_{14}H_{27}.CO_2H$
Hypogæic	Oil of ground nut	$C_{15}H_{29}.CO_2H$
Oleic	Most oils	$C_{17}H_{33}.CO_2H$
Doeglic	Doegling train oil	$C_{18}H_{35}.CO_2H$
Brassic	Colza oil (*Brassica oleifera*)	$C_{21}H_{41}.CO_2H$

Monobasic acids of the sorbic series, $C_nH_{2n-3}CO_2H$.

Tetrolic	Chlorocrotonic acid	$C_3H_3.CO_2H$
Sorbic	Mountain-ash berries	$C_5H_7.CO_2H$
Palmitolic	Hypogæic acid	$C_{15}H_{27}.CO_2H$
Stearolic	Oleic acid	$C_{17}H_{31}.CO_2H$
Behenolic	Brassic acid	$C_{21}H_{39}.CO_2H$

Monobasic acids of the benzoic series.

Benzoic	Gum benzoin	$C_6H_5.CO_2H$
Toluic	Toluene	$C_7H_7.CO_2H$
Mesitylenic	Mesitylene	$C_8H_9.CO_2H$
Cuminic	Cummin oil	$C_9H_{11}.CO_2H$
Homocuminic	,,	$C_{10}H_{13}.CO_2H$

Monobasic acids of the cinnamic series.

Cinnamic	Storax	$C_8H_7.CO_2H$
Atropic	Atropine	$C_8H_7.CO_2H$
Phenyl-crotonic		$C_9H_9.CO_2H$
Phenyl-angelic		$C_{10}H_{11}.CO_2H$
Cumenyl-acrylic		$C_{11}H_{13}.CO_2H$
Cumenyl-crotonic		$C_{12}H_{15}.CO_2H$
Cumenyl-angelic		$C_{13}H_{17}.CO_2H$

Monobasic acids of the lactic series.

Glycolic	Oxidation of glycol and of alcohol	$CH_3O.CO_2H$
Lactic	Fermentation of milk sugar	$C_2H_5O.CO_2H$

Monobasic acids of the lactic series—(continued).

Acid.	Source.	Formula.
Butylactic	Oxidation of butyl glycol	$C_3H_7O.CO_2H$
Valerolactic		$C_4H_9O.CO_2H$
Leucic	Oxidation of leucine	$C_5H_{11}O.CO_2H$

Monobasic acids of the salicylic series.

Salicylic	Oil of winter green	$C_6H_4.OH.CO_2H$
Anisic	,, anise	$C_6H_4.OCH_3.CO_2H$
Protocatechuic	Decomposition of resins by KHO	$C_6H_3(OH)_2.CO_2H$
Phloretic	,, phloretin ,,	$C_6H_3.CH_3.OCH_3.CO_2H$
Vanillic	Oxidation of vanillin	$C_6H_3.OH.OCH_3.CO_2H$
Tannic	Gall-nuts	$C_{13}H_9O_7.CO_2H$
Gallic	,,	$C_6H_2(OH)_3.CO_2H$

Monobasic acids of uncertain constitution.

Caffeic	Coffee	$C_8H_7O_2.CO_2H$
Quinic	Cinchona bark	$C_6H_{11}O_4.CO_2H$
Ellagic	Bezoar stones	$C_{13}H_9O_8.CO_2H$

Acids produced by oxidation of carbohydrates.

Saccharic	Oxidation of sugar	$C_4H_8O_4.(CO_2H)_2$
Mucic	,, gum	
Pyromucic	Distillation of mucic acid	$C_4H_3O.CO_2H$

Dibasic acids of the oxalic series.

Oxalic	Wood sorrel	$CO_2H.CO_2H$
Malonic	Oxidation of malic acid	$CH_2(CO_2H)_2$
Succinic	Amber	$C_2H_4(CO_2H)_2$
Pyrotartaric	Distillation of tartaric acid	$C_3H_6(CO_2H)_2$
Adipic	Oxidation of oleic acid	$C_4H_8(CO_2H)_2$
Pimelic	,, ,,	$C_5H_{10}(CO_2H)_2$
Suberic	,, cork	$C_6H_{12}(CO_2H)_2$
Azelaic	,, castor oil	$C_7H_{14}(CO_2H)_2$
Sebacic	Distillation of oleic acid	$C_8H_{16}(CO_2H)_2$
Brassylic	Oxidation of behenolic acid	$C_9H_{18}(CO_2H)_2$
Roccellic	*Roccella tinctoria*	$C_{15}H_{30}(CO_2H)_2$

Dibasic acids of the fumaric series.

Fumaric	Fumitory	$C_2H_2(CO_2H)_2$
Malæic	Distillation of malic acid	
Pyrocitric	,, citric acid	$C_3H_4(CO_2H)_2$
Itaconic	,, ,,	
Citraconic	,, ,,	
Mesaconic	,, ,,	
Hydromuconic	Mucic acid	$C_4H_6(CO_2H)_2$

Dibasic acids of the tartaric series.

Tartronic	Oxidation of grape sugar	$CH.OH(CO_2H)_2$
Mesoxalic	,, uric acid	$C(OH)_2(CO_2H)_2$
Malic	Unripe apples	$C_2H_3.OH(CO_2H)_2$
Tartaric	Grape juice	$C_2H_2(OH)_2(CO_2H)_2$
Racemic	,,	

Dibasic acids from oxidation of hydrocarbons.

Phthalic	Oxidation of naphthalene	$C_6H_4(CO_2H)_2$
Isouvitic	Gamboge fused with KHO	$C_7H_6(CO_2H)_2$
Cumidic	Oxidation of durene	$C_6H_2(CH_3)_2(CO_2H)_2$

Tribasic vegetable acids.

Tricarballylic	Beet-root	$C_3H_5(CO_2H)_3$
Citric	Lemon juice	$C_3H_4.OH(CO_2H)_3$
Aconitic	Monkshood	$C_3H_3(CO_2H)_3$
Meconic	Opium	$C_4HO(CO_2H)_3$

Acids containing nitrogen.

Acid.	Source.	Formula.
Hydrocyanic	Fermentation of bitter almonds	CNH
Picric	Oxidation of phenol	$C_6H_2(NO_2)_3OH$
Hippuric	Horse urine	$C_8H_8NO.CO_2H$
Uric	Human urine	$C_5H_4N_4O_3$

360. *Formic acid*, $H.CO_2H$, is prepared by distilling oxalic acid with glycerin. 30 grammes (or one ounce) of crystallised oxalic acid and 200 cubic centimetres (6.5 fluid ounces) of glycerin are heated, in a half-litre (or pint) flask provided with a thermometer and condenser, to about 80° C., when formic acid distils over together with the water of crystallisation of the oxalic acid, and carbonic acid gas is evolved; $CO_2H.CO_2H = H.CO_2H + CO_2$. When the evolution of CO_2 ceases, a fresh quantity of oxalic acid may be introduced and the operation continued, the same glycerin serving for the conversion of a large quantity of oxalic acid. The formic acid first produced converts the glycerin into *monoformin*—

$$C_3H_5(OH)_3 + H.CO_2H = C_3H_5(OH)_2(CO_2H) + HOH.$$

The monoformin is then decomposed by the water of crystallisation of the oxalic acid, the equation being reversed, and glycerin being reproduced. By continuing the process, formic acid of 56 per cent. may be obtained. To prepare the pure acid this is neutralised with lead oxide, the lead formate crystallised, dried, and heated to 100° C. in a current of dry H_2S; $(H.CO_2)_2Pb + H_2S = 2HCO_2H + PbS$. The formic acid is carefully condensed and redistilled with a little lead formate to remove H_2S.

Formic acid was originally obtained from ants. It occurs in nettles and other plants, in some animal fluids, and occasionally in mineral waters.

It has been obtained synthetically by heating caustic alkalies to 100° C. in carbonic oxide; $CO + KOH = HCO_2K$ (potassium formate); again, potassium, acting on carbon dioxide in presence of water, yields potassium dicarbonate and formate—

$$2CO_2 + H_2O + K_2 = KHCO_3 + HCO_2K.$$

Formic acid is also produced in other reactions in which carbonic acid is acted on by reducing agents. Carbonic acid may be regarded as *hydroxyformic acid*, $HO.CO_2H$, that is, formic acid, $H.CO_2H$, in which H is replaced by HO. When starch and other organic bodies are violently oxidised, they yield carbonic acid, but if they are gradually and quietly oxidised, they yield formic acid. The quiet oxidation of organic bodies is often effected by heating them with MnO_2 and dilute H_2SO_4.

Properties of formic acid.—Colourless liquid, fuming slightly in air and of pungent smell; it blisters the skin. Formic acid boils at 99°.9 C. and solidifies at 8°.6. Its sp. gr. is 1.22 at 20°. The diluted acid boils at a higher temperature; an acid of 77 per cent. boils at 107°.

The *formates* are all soluble in water; their solutions yield a red colour with ferric chloride, and reduce silver from the nitrate, when boiled with it, on account of the tendency of formic acid to become carbonic (hydroxyformic). Solid formates evolve carbonic oxide (burning with a blue flame) when heated with strong H_2SO_4, which removes the elements of water; $H.CO_2H = HOH + CO$. A formate heated with excess of baryta yields the oxalate; $(HCO_2)_2Ba = (CO_2)_2Ba + H_2$.

Formic acid is used in making some of the coal-tar dyes.

361. *Acetic acid*, or *methyl-formic acid*, $CH_3.CO_2H$, is obtained by the destructive distillation of wood or of sawdust, or spent dye-woods. The aqueous layer in the condenser (p. 491) is neutralised by sodium carbonate, and the methyl-alcohol and acetone are distilled off. The evaporated liquor deposits impure crystals of sodium acetate, which is heated to expel some tarry matters, and distilled with sulphuric acid, when acetic acid passes over—

$$CH_3.CO_2Na + H_2SO_4 = CH_3.CO_2H + NaHSO_4.$$

The crude acid from wood is termed *pyroligneous acid.*

Acetic acid is also made by the oxidation of alcohol for the production of vinegar. $CH_3.CH_2.OH$ (ethyl-alcohol) $+ O_2 = CH_3.CO_2H + H_2O$. But this equation cannot be realised unless some third substance be present. It was seen at p. 489 that platinum black would answer the purpose, and in some chemical works this process has been employed for making acetic acid. Weak fermented liquors, such as beer and the lighter wines, are very liable to become sour, which is never the case with distilled spirits, however much diluted. This is due to the presence in the fermented liquid of albuminous (nitrogenised) matters and salts, which afford nourishment to a microscopic organism, termed *Mycoderma aceti*, which appears to convey the oxygen of the air to the alcohol.

Quick vinegar process.—A weak spirit mixed with a little yeast or beet-root juice, heated to about 27° C., is caused to trickle slowly from pieces of cord fixed in a perforated shelf over a quantity of wood shavings previously soaked in vinegar to impregnate them with the mycoderm or acetic ferment. The shavings are packed in a tall cask (fig. 278) in which holes have been drilled in order to allow the passage of air. The oxidation of the alcohol soon raises the temperature to about 38° C., which occasions a free circulation of air among the shavings. The mixture is passed three or four times through the cask, and in about thirty-six hours the conversion into vinegar is completed. If the supply of air be insufficient, alcohol is lost in the form of aldehyd vapour, the irritating odour of which pervades the air of the factory.

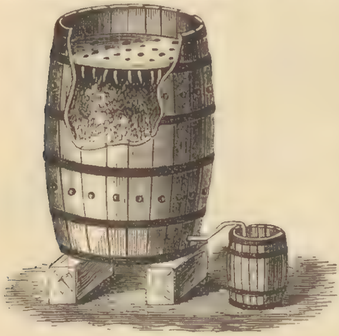
Fig. 278.

White-wine vinegar is prepared from light wines by a similar process.

Malt vinegar is made from infusion of malt fermented by yeast with free contact of air.

Vinegar contains, on an average, about 5 per cent. of acetic acid. Its aroma is due to the presence of a little acetic ether. The vinegar of commerce is allowed to be mixed with $\frac{1}{1000}$th of its weight of sulphuric acid in order to prevent it from becoming mouldy.

By distilling vinegar, a weak acetic acid is obtained, which may be concentrated by re-distilling and receiving separately the portion distilling between 110° and 120° C.

Pure acetic acid is prepared by distilling 5 parts by weight of fused sodium acetate with 6 parts of concentrated sulphuric acid;

$$CH_3.CO_2Na + H_2SO_4 = CH_3.CO_2H + NaHSO_4.$$

The distillate may be redistilled with a little MnO_2 to remove SO_2.

Properties of acetic acid.—Colourless, pleasant smell, blistering the skin, boiling at 118° C., and giving a vapour which burns with a flame like that of alcohol. Its true melting point is 17° C., but it may be cooled far below this without solidifying, unless a crystal of the acid be introduced, when the whole crystallises in beautiful plates; hence the term *glacial acetic acid*. The sp. gr. of the pure acid is 1.063 at 18°, but the strength of the acid cannot, as in other cases, be inferred from the sp. gr., because the latter is increased by addition of water, till it reaches 1.079 (70 per cent. of acid), when it is diminished by more water, so that a weak acid may have the same sp. gr. as the pure acid.

Acetic acid is one of the most stable of the organic acids. It is unacted on by most oxidising agents. When its vapour is passed through a red-hot tube, it yields several products, among which marsh gas and acetone are conspicuous. Most of its salts are soluble in water, so that it is not easily precipitated; but if it be exactly neutralised by ammonia, and stirred with silver nitrate, a crystalline precipitate of *silver acetate*, $CH_3.CO_2Ag$, is obtained; *mercurous acetate*, $CH_3.CO_2Hg$, may be obtained in a similar way. Ferric chloride added to the neutral solution gives a fine red colour.

362. Many of the acetates are employed in the arts. Those formed by the weaker bases, such as Fe_2O_3 and Al_2O_3, are easily decomposed by boiling with water, basic acetates being precipitated; hence the *aluminium acetate* and *ferric acetate* (*red liquor*) are much used by dyers and calico-printers as *mordants*, the basic acetates being deposited in the fabric, and forming insoluble compounds with colouring matters.

Lead acetate, or *sugar of lead*, $(CH_3CO_2)_2Pb.3Aq$, is the commonest commercial acetate, and is prepared by dissolving litharge (PbO) in an excess of acetic acid, when the solution deposits prismatic crystals of the salt. On the large scale, acetic acid vapour is passed through copper vessels with perforated shelves on which litharge is placed. Lead acetate is intensely sweet and very soluble in water (1½ part). Commonly, the solution is turbid from the precipitation of lead carbonate by the carbonic acid in the water; a drop of acetic acid clears it. The acetate is soluble in alcohol. When heated, it fuses at 75° C. and becomes anhydrous at 100°. The anhydrous salt melts when further heated, evolves the pleasant smell of acetone, and becomes again solid as a basic lead acetate, which is decomposed at a higher temperature, evolving CO_2 and acetone, and leaving a yellow residue of PbO mixed with globules of lead.

There are several basic lead acetates, but the only one of practical importance is the *tribasic lead acetate*, or *Goulard's extract*, $(CH_3.CO_2)_2Pb.2PbO.H_2O$, which is prepared by boiling lead acetate with litharge. It forms needle-like crystals which are very soluble in water, but insoluble in alcohol. A strong solution of the salt is not affected by the air, but a weak solution is rendered turbid by the smallest quantity of CO_2 in air or water. Tribasic lead acetate is very useful in the laboratory for precipitating tannin, gum, &c., from vegetable infusions in order to extract the alkaloids.

Verdigris is a mixture of several basic cupric acetates prepared by acting on sheet copper with the refuse grapes of the wine-press, which yield acetic acid by oxidation of the alcohol; the acid combines with the cupric oxide formed by the action of air upon the copper. Commercial verdigris consists chiefly of the compound $(CH_3.CO_2)_2Cu.CuO.6H_2O$. When this is treated with water it is only partly dissolved, the residue having the composition $(CH_3.CO_2)_2Cu.2CuO.2H_2O$. By dissolving verdigris in acetic acid, the normal cupric acetate may be obtained in crystals of the formula $(CH_3.CO_2)_2Cu.H_2O$. It forms blue prisms soluble in water. Verdigris is used in the manufacture of colours, and in dyeing and calico-printing.

Emerald-green, or *cupric aceto-arsenite*, $(CH_3.CO_2)_2Cu.Cu_3(AsO_3)_2.2As_2O_3$, is made by boiling verdigris with white arsenic and water. It is used for colouring wall-paper and other fabrics, and is dangerous to the makers and purchasers.

Sodium acetate, $CH_3.CO_2Na.3Aq$, prepared by neutralising acetic acid with sodium carbonate, crystallises in prisms which are very soluble in water, and yield one of the best examples of a supersaturated solution (see p. 43), which is used in foot-warmers for railway carriages, on account of the continuous evolution of heat during its crystallisation. It is four times as effective as an equal volume of water.

The acetates of sodium and potassium are remarkable for their fusibility and their stability at high temperatures; they do not carbonise like most salts of organic acids. Potassium, sodium, and ammonium acetates combine with one and with two molecules of acetic acid to form crystalline compounds.

Calcium acetate, when dissolved in water together with $CaCl_2$, yields the compound $CH_3.CO_2.ClCa.5Aq$, which crystallises easily, and is sometimes produced for effecting the purification of crude acetic acid (Condy's patent).

Zinc acetate, $(CH_3.CO_2)_2Zn.3Aq$, is remarkable for being capable of sublimation at a moderate heat, when dried.

Acetic acid is very useful in organic chemistry as a simple solvent, especially for resins and hydrocarbons, such as naphthalene and anthracene.

This acid is found, either free or combined, in many plants and in some animal fluids. It is usually among the final products of the oxidation of bodies containing the methyl group.

363. Acetic acid has been produced synthetically by the following reactions:—(1) C heated in vapour of S yields CS_2. (2) Vapour of CS_2 mixed with Cl and passed through a red-hot tube—

$$CS_2 + 3Cl_2 = S_2Cl_2 + CCl_4.$$

(3) Vapour of CCl_4 passed through a red-hot tube yields chlorine and *tetrachlorethene;* C_2Cl_4. (4) C_2Cl_4 acted on by Cl and water, in sunlight; $C_2Cl_4 + Cl_2 + 2H_2O = 3HCl + CCl_3.CO_2H$ (trichloracetic acid). (5) When this last is acted on by nascent hydrogen (sodium-amalgam and water), it yields acetic acid; $CCl_3.CO_2H + H_6 = CH_3.CO_2H + 3HCl$.

Acetic acid may also be produced from methane by the action of carbon oxychloride, which converts it into acetyl chloride, furnishing acetic acid when decomposed by water—

$$CH_4 + COCl_2 = CH_3.CO.Cl + HCl. \qquad CH_3.CO.Cl + HOH = CH_3.CO.OH + HCl.$$

Acetic oxychloride, or *acetyl chloride*, $CH_3.COCl$, is obtained by distilling glacial acetic acid (3 parts) with phosphorus trichloride (2 parts) at a steam heat, in a retort furnished with a condenser, both carefully dried; $3CH_3COOH + 2PCl_3 = P_2O_3 + 3HCl + 3CH_3COCl$. The acetyl chloride is a very pungent fuming liquid of sp. gr. 1.125, and boiling point 55°. It is decomposed by water as above. This renders it a very valuable agent for effecting the replacement of hydroxyl by chlorine, as in the equation referred to it has converted H.OH into HCl.

The group $CH_3.CO$, which remains unchanged during these reactions, is termed *acetyl*, C_2H_3O, and may be regarded as ethyl, C_2H_5, in which H_2 have been replaced by O''. This allows us to write ethyl as $C_2H_3.H_2$, or $CH_3.CH_2$, to indicate the different relations of the two portions of H. Thence, the formula of ethyl-alcohol would become $CH_3.CH_2.OH$, and the formation of acetic acid by its oxidation would consist in the conversion of the group $CH_2.OH$ into $CO.OH$. Similar views may be entertained respecting the other monohydric alcohols, each *alcohol radical* having a corresponding *acid radical* containing the same number of carbon atoms, but having an oxygen atom in place of two hydrogen atoms; a few examples are here given—

Alcohol radicals,		*Acid radicals,*	
C_nH_{2n+1}.		$C_nH_{2n-1}O$.	
Methyl	CH_3	Formyl	CHO
Ethyl	$CH_3.CH_2$	Acetyl	$CH_3.CO$
Propyl	$C_2H_5.CH_2$	Propionyl	$C_2H_5.CO$
Butyl	$C_3H_7.CH_2$	Butyryl	$C_3H_7.CO$
Amyl	$C_4H_9.CH_2$	Valeryl	$C_4H_9.CO$

364. *Acetic anhydride*, or *di-acetyl oxide*, or *anhydrous acetic acid*, $(CH_3.CO)_2O$, is prepared by distilling acetyl chloride with an equal weight of perfectly anhydrous sodium acetate; $CH_3.CO.Cl + CH_3.CO.ONa = (CH_3.CO)_2O + NaCl$. It distils over as a colourless liquid, smelling of acetic acid, but irritating the eyes; its sp. gr. is 1.073, and boiling point 138° C. It dissolves slowly in water, with evolution of heat and formation of acetic acid—

$$(CH_3.CO)_2O \ + \ H_2O \ = \ 2(CH_3.CO.OH).$$

Acetic anhydride may also be formed by heating lead acetate with carbon disulphide; $2Pb(CH_3.CO_2)_2 + CS_2 = 2(CH_3.CO)_2O + 2PbS + CO_2$.

By carefully acting on acetic anhydride with sodium-amalgam and water (or snow), it has been converted into aldehyd and alcohol—

$$(CH_3.CO)_2O + 2H_2 = 2(CH_3.COH) + H_2O. \quad CH_3.COH + H_2 = CH_3.CH_2.OH.$$

Hence, aldehyd is sometimes termed *acetyl hydride*.

Acetyl dioxide, or *acetic peroxide*, $(CH_3.CO)_2O_2$, is obtained by adding barium dioxide to an ethereal solution of acetic anhydride—

$$2(CH_3.CO)_2O \ + \ BaO_2 \ = \ (CH_3.CO)_2O_2 \ + \ Ba(CH_3.CO_2)_2.$$

It is an oily liquid, insoluble in water, and exploding violently when heated. It has the powerful oxidising properties which would be expected from its chemical resemblance to hydric peroxide.

365. *Propylic* or *propionic acid*, $C_2H_5.CO_2H$, is not produced upon a large scale like acetic acid. It is formed in the putrefaction of various organic bodies, and in the destructive distillation of wood and of rosin. It may be separated from formic and acetic acids by saturating the mixture with PbO, evaporating to dryness, and extracting with cold water. On boiling the solution, it deposits *basic lead propylate*, leaving the basic lead formate and acetate in solution. From the lead-salt, the acid may be obtained by the action of H_2S or H_2SO_4.

Sodium propylate is obtained by the action of CO upon sodium ethylate, just as sodium formate is obtained from sodium hydrate (see p. 509)—

$$CO \ + \ C_2H_5.ONa \ = \ C_2H_5.CO_2Na.$$

Propylic acid, as would be expected, resembles acetic acid. Its sp. gr. is .99, and it boils at 142° C. It has no practical importance. The propylates are mostly soluble in water, but silver propylate is sparingly soluble. Lead propylate is much more difficult to crystallise than lead acetate.

Butyric acid, $C_3H_7.CO_2.H$, is made from cane-sugar by dissolving it in water (5 parts), adding a little tartaric acid ($\frac{1}{200}$th part), and boiling, to convert the sucrose into glucose, and adding to the cooled liquid some putrid cheese ($\frac{1}{25}$th part) rubbed up in about thirty times its weight of milk. Some chalk ($\frac{1}{2}$ part) is stirred into the mixture, which is then allowed to ferment for a week at a temperature of 30–35° C. The glucose, $C_6H_{12}O_6$, undergoes the *lactic fermentation*, and is converted into lactic acid, $C_3H_6O_3$, which is converted, by the chalk, into calcium lactate, forming a pasty mass of crystals. After a time, the mass becomes liquid again, evolving bubbles of hydrogen and carbon dioxide, and forming a strong solution of calcium butyrate. When this is mixed with strong hydrochloric acid, the butyric acid rises to the surface and forms an oily layer, which may be purified by distillation. The passage of lactic acid into butyric acid is expressed by the equation $2C_3H_6O_3 = C_3H_7.CO_2H + 2CO_2 + 2H_2$.

Butyric acid is a strongly acid liquid, smelling of rancid butter, having the sp. gr. 0.96, and boiling at 163° C. It mixes readily with water, but separates again when the water is saturated with a salt. The butyrates are rather less soluble than the acetates. Calcium butyrate is less soluble in hot water than in cold. Silver butyrate is very sparingly soluble.

Butyric acid is found in the products of distillation of wood and of some other organic bodies. It exists in the perspiration of the skin, and, as a glyceride, in butter, in cod-liver oil, and in some vegetable oils.

Valeric, or *valerianic*, or *isopentoic acid*, $C_4H_9.CO_2H$, is prepared by oxidising amyl-alcohol (fousel oil) with potassium dichromate and sulphuric acid. One part of amyl-alcohol is slowly mixed with four parts of sulphuric acid, and the cold mixture gradually added to five parts of potassium dichromate and four parts of water in a flask or retort with an inverted condenser. When the lively action ceases, the mixture is boiled as long as oily drops (isovaleric aldehyd) appear in the condenser; the latter is then reversed, and the distillation proceeded with. The distillate contains water, valeric acid, and amyl valerate; it is shaken with a slight excess of soda, when the amyl valerate rises to the surface ; the aqueous layer is evaporated to dryness, and the sodium valerate decomposed by $\frac{4}{5}$ths of its weight of sulphuric acid diluted with half its weight of water ; the valeric acid rises to the surface, and is rectified over fused calcium chloride.

The oxygen furnished by the potassium dichromate and sulphuric acid (see p. 501) converts the amyl-alcohol into valeric acid, according to the equation $C_4H_9.CH_2.OH + O_2 = C_4H_9.CO.OH + H_2O$.

Valeric acid is an oily liquid smelling like old cheese ; its sp. gr. is .95, and it boils at 175° C. It is much less soluble in water than the preceding acids, requiring thirty times its weight.

The valerates are, as a rule, easily soluble in water, but the silver salt is sparingly soluble. Zinc valerate is used medicinally.

Valeric acid occurs in valerian root, in the elder, in the berries of the guelder rose, and in many other plants ; also in some fish oils and in the perspiration.

Caproic or *hexoic acid*, $C_5H_{11}.CO_2H$, is found in butter from cows and goats, and in Limberg cheese, being one cause of its odour ; it is also found in some plants, and in the perspiration. Caproic acid is formed, together with butyric and acetic acids, in the butyric fermentation described at page 513. It may be separated from these by fractional distillation. Caproic acid has the sp. gr. .94, and boils at 205°. It dissolves very sparingly in water, and has a repulsive odour.

The caproates of barium and calcium are rather sparingly soluble in water, and silver caproate is nearly insoluble.

366. *Œnanthic* or *heptoic acid*, $C_6H_{13}.CO_2H$, is found among the products of the distillation of fats by superheated steam. It may also be obtained by oxidising œnanthic aldehyd (œnanthol) with potassium dichromate and sulphuric acid.

Œnanthic acid has a faint odour and sp. gr. .93 ; it boils at 223° C. Many of the œnanthates are nearly insoluble in water. The strong solutions of the alkaline œnanthates become gelatinous on cooling, like solution of soap.

Caprylic or *octoic acid*, $C_7H_{15}.CO_2H$, is found in the fousel oil from wines, in old cheese, and, as a glyceride, in butter, human fat, and cocoa-nut oil.

Caprylic acid is the first acid of this series which is solid at common temperatures, forming needle-like crystals or scales fusible at about 16° C. and boiling at 233°. It has an offensive smell, and is very sparingly soluble in water.

The caprylates, except those of the alkalies, are sparingly soluble in water, but they dissolve in alcohol.

Pelargonic or *nonoic acid*, $C_8H_{17}.CO_2H$, was originally obtained from the essential oil of *Pelargonium roseum*, and is found among the products of oxidation of oleic acid by nitric acid. It is also formed when essential oil of rue, rutic aldehyd, $C_9H_{19}.COH$, is oxidised by nitric acid.

Pelargonic acid is an oily liquid, of faint odour, crystallising at 12° C. and boiling at 253°. It has the sp. gr. .91 and is insoluble in water. The pelargonates are sparingly soluble in water, except those of the alkalies.

Rutic, *capric*, or *decatoic acid*, $C_9H_{19}.CO_2H$, may be obtained from many fats, and by the oxidation of oleic and other fatty acids. It has a smell of goats ; forms crystals which fuse at 30° C. and boil at 270°. It dissolves slightly in boiling water, and crystallises out on cooling.

Euodic, *hendecatoic*, or *undecylic acid*, $C_{10}H_{21}.CO_2H$, is formed when oil of rue is oxidised. Its fusing point is 30° C. It cannot be boiled without decomposition, except under diminished pressure.

Lauric or *dodecatoic acid*, $C_{11}H_{23}.CO_2H$, is obtained from a fatty substance found in the fruit of the sweet bay (*Laurus nobilis*) and in *sassafras-nuts* or *pichurim beans*, which are used for flavouring chocolate, and are the seeds of another of the Lauraceæ (*Nectandra puchury*). A similar substance is found in the mango and in a variety of cochineal insect. The fat is saponified by boiling with potash, the solution decomposed by hydrochloric acid, and the separated fatty acid distilled, when lauric acid is found in the first fractions.

The crystals of lauric acid fuse at 44° C. It cannot be distilled at ordinary pressures without decomposition.

Cocinic or *tridecylic acid*, $C_{12}H_{25}.CO_2H$, originally obtained, in small quantity, from cocoa-nut oil, is a crystalline solid, fusing at 45°. It has no practical importance.

Myristic acid, $C_{13}H_{27}.CO_2H$, occurs as a glyceride in nutmeg-butter, the fatty substance extracted from powdered nutmegs by boiling with ether. It may be extracted by a process similar to that employed for lauric acid. Its alcoholic solution deposits it in needles fusing at 54° C.

Myristic acid has also been obtained from the fatty matter of the mango, and, in small quantity, from cocoa-nut oil.

Pentadecylic acid, $C_{11}H_{29}.CO_2H$, has been obtained from the fungus, *Agaricus integer;* its crystals fuse at about 70° C.

367. *Palmitic acid*, $C_{15}H_{31}.CO_2H$, is the first of the *fatty acids*, properly so called, which occur as glycerides in the vegetable and animal fats, and form true *soaps* with the alkalies, such soaps being the salts formed by the fatty acid with the alkali-metal, characterised by easily *lathering* when dissolved in soft water, by being precipitated from their aqueous solutions by common salt, and by giving an oily layer of the melted fatty acid when boiled with any of the common acids.

On the large scale, palmitic acid is made from palm-oil, as described at p. 496. It has also lately been manufactured by the action of potassium hydrate on oleic acid.

On the small scale, the palm-oil is boiled with potash, which converts it into potassium palmitate and oleate; on adding dilute sulphuric acid to the solution, a mixture of palmitic and oleic acids is precipitated; this is washed, dried, and dissolved in hot alcohol, from which the palmitic acid crystallises on cooling, leaving the oleic acid in solution. Palm-oil contains the glycerides palmitin and olein, which are *saponified* by the potash, with liberation of glycerin, as will be further explained under the head of *Ethereal salts*, to which the glycerides belong.

Palmitic acid crystallises in needles which fuse at 62° C. It is decomposed by distillation, except in the presence of steam.

The substance known as *adipocere*, a wax-like mass which is left when animal bodies decompose in the earth, is a mixture of palmitates of calcium and potassium.

The formation of palmitic acid from spermaceti has been explained at p. 493.

Margaric acid, $C_{16}H_{33}.CO_2H$, is synthetically obtained by processes which will be referred to hereafter. The substance formerly known by this name, and supposed to exist as the glyceride *margarin* in natural fats, proved to be a mixture of stearic and palmitic acids. Margaric acid crystallises like palmitic, and fuses at 60° C.

Stearic acid, $C_{17}H_{35}.CO_2H$, may be prepared from suet by boiling it with potash, decomposing the resulting soap with hydrochloric acid, drying the separated fatty acids, and dissolving in the least possible quantity of hot alcohol. This retains the oleic acid in solution and deposits a mixture of stearic and palmitic acids on cooling; the mixture is well pressed in blotting-paper, and repeatedly crystallised from alcohol till it fuses at 69° C. The stearic acid exists in the suet and in most other solid fats, in the form of the glyceride stearin, mixed with palmitin and a little olein. When saponified by the potash, these yield the stearate, palmitate, and oleate of potassium.

Stearic acid is a white crystalline solid, of the same sp. gr. as water, fusing at 69° C. and not distilling without partial decomposition, except at low pressures or in a current of superheated steam. It is insoluble in water, but dissolves in alcohol and ether. It burns with a luminous flame. The alkalies dissolve stearic acid on heating, forming stearates, which are components of ordinary soaps. *White curd soap* made from tallow and soda consists chiefly of *sodium stearate*, $C_{17}H_{35}.CO_2Na$, which may be crystallised from alcohol. It dissolves in a little water to a clear solution, but when this is largely diluted it deposits scaly crystals of the *acid sodium stearate*, $(C_{17}H_{35}.CO_2)_2HNa$. Potassium stearate behaves in a similar way. The other stearates are insoluble. Those of calcium and magnesium are precipitated when hard water is brought in contact with soap. Magnesium stearate may be crystallised from alcohol.

Stearic acid mixed with palmitic acid is the material of the so-called *stearin candles.*

Balenic acid is of no practical importance.

Butic or *arachidic acid*, $C_{19}H_{39}.CO_2H$, occurs in butter, and in the Indian *Katchung oil* used for burning and dressing cloth, which is obtained from the seeds of a leguminous plant known as *Arachis hypogæa* or *ground-nut*. It is a crystalline solid fusing at 75° C.

Nardic or *medullic acid*, $C_{20}H_{41}.CO_2H$, occurs in the fat of beef. It fuses at 72°.5 C.

Behenic acid, $C_{21}H_{43}.CO_2H$, is obtained from Ben-oil, used by perfumers and watch-makers, and extracted from Ben-nuts, the seeds of the horse-radish tree (*Moringa oleifera*) of the East Indies. Its fusing point is 76° C.

Lignoceric acid, $C_{23}H_{47}.CO_2H$, obtained from beech-wood tar, crystallises in needles fusing at 80°.5 C.

Hyænic acid, $C_{24}H_{49}.CO_2H$, prepared from the fat of the hyæna, fuses at 77° C.

Cerotic acid, $C_{26}H_{53}.CO_2H$(?), forms about two-thirds of bees'-wax, and may be extracted from it by boiling alcohol, which deposits the acid on cooling. It fuses at 79° C.

Cerotic acid is, according to recent statements, a mixture of two acids, one of which is $C_{33}H_{67}.CO_2H$, fusing at 91° C.

Melissic acid, $C_{29}H_{59}.CO_2H$, is obtained by the oxidation of the corresponding alcohol (p. 493) obtained from different varieties of wax. It fuses at 91° C.

368. *General remarks on the acetic series of acids.*—It will have been noticed that, as the number of carbon atoms in the acids increases, their solubility in water diminishes. Acetic acid mixes with water in all proportions, while palmitic acid is quite insoluble. In a similar way, the volatility of the acids decreases, so that palmitic acid and those richer in carbon can only be distilled under diminished pressure or in a current of steam.

The acid strength also diminishes with the increase in the carbon atoms, and this is turned to account in separating the volatile fatty acids from each other by the *method of partial saturation*. Suppose it to be required to separate butyric and valeric acids. The mixture is divided into two equal parts, one of which is exactly neutralised by soda, yielding butyrate and valerate of sodium. The other half of the acid mixture is then added, and the whole distilled. Since butyric acid is the stronger acid, it will expel the valeric acid from the sodium valerate. If the mixture contained equal molecules of the two acids, the distillate would contain valeric acid only, and the residue would contain the sodium butyrate. If the valeric acid preponderated, the residue would contain both valerate and butyrate, and, when distilled with sulphuric acid, would yield a fresh mixture of the acids, which could be again treated in the same way. But if butyric acid preponderated, the residue would be only sodium butyrate, while the distillate would contain both butyric and valeric acids, to be again treated by partial saturation.

The non-volatile fatty acids may be separated from each other by *fractional precipitation*, which depends on the principle that the insolubility of their salts with barium, magnesium, and lead increases with the number of carbon atoms. The mixture of fatty acids is dissolved in alcohol, and is *partially* precipitated by an alcoholic solution of the acetate of Ba, Mg, or Pb. This precipitate will contain the acid or acids richest in carbon. It is filtered off, and another precipitate is obtained from the solution in the same way. This will contain acids with less carbon, and so on.

Each precipitate is decomposed by HCl, and the new mixture of acids so obtained is subjected to the same treatment, until the separated acid is found to have a constant melting point.

The constitution of the fatty acids is disclosed when they are subjected to electrolysis, for they then evolve one atom of carbon as CO_2; thus, acetic acid yields dimethyl (ethane), CO_2 and H—

$$2(CH_3.CO_2.H) = (CH_3)_2 + 2CO_2 + H_2.$$

Again, valeric acid yields dibutyl, CO_2 and H—

$$2(C_4H_9.CO_2.H) = (C_4H_9)_2 + 2CO_2 + H_2.$$

369. *Acrylic acid*, $C_2H_3.CO_2H$, is obtained by heating acrolein (p. 503) with water and silver oxide in the dark; $C_2H_3.COH + Ag_2O = C_2H_3.CO_2H + Ag_2$. It is a pungent liquid, miscible with water, and boiling at 140° C. Nascent hydrogen converts it into propylic acid, $C_2H_5.CO_2H$. Potassium acrylate, fused with potassium hydrate, yields acetate and formate of potassium—

$$C_2H_3.CO_2K + KOH + H_2O = CH_3.CO_2K + H.CO_2K + H_2.$$

Crotonic acid, $C_3H_5.CO_2H$, was so called because a substance isomeric with it was obtained from croton oil. It may be obtained by oxidising crotonic aldehyd with silver oxide (see p. 503). It is a crystalline solid, fusing at 72° C. and boiling at 189°, its vapour condensing in scales. It is moderately soluble in water, and has an odour like butyric acid. Nascent hydrogen converts it into butyric acid; $C_3H_5.CO_2H + 2H = C_3H_7.CO_2H$. Fused potash converts it into potassium acetate; $C_3H_5.CO_2H + 2KOH = 2(CH_3.CO_2K) + H_2$. Nitric acid converts it into acetic and oxalic acids, by oxidation; $C_3H_5.CO_2H + O_4 = CH_3.CO_2H + CO_2H.CO_2H$. Chromic acid carries the oxidation a step farther, producing acetic acid, water, and carbon dioxide; $C_3H_5.CO_2H + O_5 = CH_3.CO_2H + 2CO_2 + H_2O$. Crotonic acid has been found in crude pyroligneous acid.

Angelic acid, $C_4H_7.CO_2H$, is obtained by boiling angelica root (an umbelliferous plant) with lime and water, filtering, acidifying with sulphuric acid, and distilling. The acid appears to be contained in the root as an ethereal salt, which is decomposed by the lime. Chamomile flowers and some other aromatic plants also yield this acid.

Angelic acid crystallises in prisms, fusing at 45° C. and boiling at 185°. It has an aromatic odour, is soluble in hot water and in alcohol and ether. When boiled for some time, it is converted into an isomeride, *tiglic acid* or *methyl-crotonic acid*, $C_3H_4.CH_3.CO_2H$, which is also obtained from croton oil (*Croton tiglium*), and, together with angelic acid, from cummin oil (*Cuminum cyminum*). Fused with potash, angelic acid yields acetate and propylate of potassium—

$$C_4H_7.CO_2H + 2KOH = CH_3.CO_2K + C_2H_5.CO_2K + H_2.$$

Pyroterebic acid, $C_5H_9.CO_2H$, is prepared by distilling terebic acid, a product of the action of nitric acid on turpentine; $C_6H_9O_2.CO_2H = C_5H_9.CO_2H + CO_2$. Pyroterebic acid is a liquid boiling at 210° C., and having a characteristic odour. Fused potash converts it into acetate and (iso)butyrate of potassium—

$$C_5H_9.CO_2H + 2KOH = CH_3.CO_2K + C_3H_7.CO_2K + H_2.$$

Damaluric acid, $C_6H_{11}.CO_2H$, occurs in small quantity in the urine of men, horses, and cows. It is liquid, and smells like valeric acid. It is little known.

Campholic acid, $C_9H_{17}.CO_2H$, also little known, is obtained by boiling camphor with alcoholic solution of potash; $C_{10}H_{16}O + KOH = C_9H_{17}.CO_2K$. By evaporating the alcohol, dissolving the potassium campholate in water, and adding HCl, the campholic acid is precipitated, and may be crystallised from alcohol. It is a volatile acid, and fuses at 95° C.

Cimicic acid, $C_{14}H_{27}.CO_2H$, exists in a stinging beetle, the *tree-bug* (*cimex*); by treating the beetles with ether, the acid is extracted, and crystallises from the solution in prisms fusing at 44° C.

Hypogæic acid, $C_{15}H_{29}.CO_2H$, is extracted from the ground-nut, together with butic acid (see p. 516). It is crystalline, fuses at 33° C., and dissolves in alcohol and ether. It is worth notice that hypogæic acid absorbs oxygen from air.

Physetoleic acid, isomeric with hypogæic, is obtained from spermaceti oil. It differs from hypogæic by fusing at 30° C., and by not yielding sebacic acid when distilled. Another isomeride, *gaidic acid*, is formed by the action of N_2O_3 on hypogæic acid. It fuses at 39° C., does not oxidise in air, and distils undecomposed.

370. *Oleic acid*, $C_{17}H_{33}.CO_2H$, the most important member of the acrylic series of acids, is prepared by boiling olive-oil with potash, and decomposing the solution with hydrochloric acid, which separates the oleic acid as an oily layer which contains some stearic and palmitic acids. To purify it, it is heated with litharge to 100° C. for some hours, when a mixture of oleate, palmitate, and stearate of lead is obtained. The oleate is extracted from this mixture by ether, and the solution shaken with hydrochloric acid, which precipitates the lead as chloride, while the oleic acid remains dissolved in the ether, which rises to the surface. The ether is distilled off, the impure oleic acid is dissolved in ammonia, and precipitated by barium chloride; the barium oleate is recrystallised from alcohol, and decomposed by tartaric acid to separate the oleic acid.

The olive-oil contains the glyceride *olein*, which is decomposed by boiling with potash into glycerin and potassium oleate. Olein is a general constituent of the fixed oils; the *soft soap* made by saponifying whale and seal oils with potash consists chiefly of potassium oleate. Oleic acid is a by-product in the manufacture of candles, in which its presence would be injurious by lowering the fusing point. It is used in greasing wool for spinning, being much more easily removed by alkalies than olive-oil, which was formerly employed. Ammonium oleate is sometimes employed as a mordant for the anilin dyes on cotton.

Oleic acid is an oily liquid which crystallises at 0° C. and fuses again at 14°. When distilled, it yields a number of products of decomposition, among which *sebacic acid*, $C_8H_{16}(CO_2H)_2$, is conspicuous. In a current of superheated steam, at 250° C., it may be distilled without decomposition. In its commonly impure state, it absorbs oxygen readily when exposed to air.

Fusion with potash converts oleic acid into acetate and palmitate of potassium; $C_{17}H_{33}.CO_2H + 2KOH = CH_3.CO_2K + C_{15}H_{31}.CO_2K + H_2$. By the action of N_2O_3, oleic acid is converted into the isomeric *elaidic acid*, which is crystalline, and fuses at 45° C. When oxidised by nitric acid, oleic acid yields several acids of the acetic and oxalic series. When heated with amorphous phosphorus and strong hydriodic acid to about 200° C., it yields stearic acid, $C_{17}H_{35}.CO_2H$.

The alkaline oleates are decomposed by much water into free alkalies and insoluble acid oleates. *Sodium oleate* is present in ordinary soap, and may be crystallised from absolute alcohol.

Barium oleate is a crystalline powder, insoluble in water, and sparingly soluble in boiling alcohol. *Lead oleate*, which forms the chief part of *lead plaster*, fuses at 80° C., and solidifies on cooling to a translucent brittle mass.

Doeglic acid, $C_{18}H_{35}.CO_2H$, is found as a glyceride in *doegling train oil* obtained from the bottle-nosed whale. It is liquid above 16° C.

Brassic or *erucic acid*, $C_{21}H_{41}.CO_2H$, may be extracted from the seeds of mustard, rape (colza), and grapes. It forms crystals which fuse at 34° C. Fusion with potash converts it into acetate and butate of potassium; $C_{21}H_{11}.CO_2H + 2KOH = CH_3.CO_2K + C_{19}H_{39}.CO_2K + H_2$. When heated with phosphorus and hydriodic acid, it gives behenic acid, $C_{21}H_{43}.CO_2H$.

371 *General remarks on the acrylic series of acids.*—It will be noticed that the acids of the acrylic series, when fused with potash, yield the potassium salts of two acids, one of which is always acetic, and the other is some member of the acetic series. The higher members of the series are characterised by their conversion into crystalline isomerides by the action of N_2O_3, and by their yielding acids of the acetic series when treated with phosphorus and hydriodic acid.

The acids of the acrylic series are able, as a rule, to combine with two atoms of bromine to form dibromo-substitution products of acids of the acetic series; thus, acrylic acid, $C_2H_3.CO_2H$, yields *dibromopropylic acid*, $C_2H_3Br_2.CO_2H$; oleic, $C_{17}H_{33}.CO_2H$, yields *dibromostearic acid*, $C_{17}H_{33}Br_2.CO_2H$. When these dibromo acids are boiled with alcoholic solution of potash, they are converted into monobromo-substitution products of the acrylic series; thus—

$$C_2H_3Br_2.CO_2H + KOH = KBr + C_2H_2Br.CO_2H + H_2O$$

—that is, dibromopropylic acid yields bromacrylic acid; or both atoms of Br may be removed as HBr, and a new acid of the sorbic series produced; thus, $\underset{\text{Dibromostearic acid.}}{C_{17}H_{33}Br_2.CO_2H} = 2HBr + \underset{\text{Stearolic acid.}}{C_{17}H_{31}.CO_2H}$

372. *Tetrolic acid*, $C_3H_3.CO_2H$, has no practical importance. It is produced when chlorocrotonic acid is heated to 100° C. with potash dissolved in alcohol: $C_3H_4Cl.CO_2H + 2KOH = C_3H_3.CO_2K + KCl + 2H_2O$. It is also formed by heating sodium allylide in carbon dioxide; $C_3H_3Na + CO_2 = C_3H_3.CO_2Na$.

Tetrolic acid is crystalline and deliquescent, fusing at 76°.5 C. and boiling at 203°. A higher temperature decomposes it into CO_2 and C_3H_4, allylene. It dissolves in alcohol and ether. Silver tetrolate undergoes spontaneous decomposition into CO_2 and silver allylide.

Sorbic acid, $C_5H_7.CO_2H$, is obtained by distilling the juice of unripe mountain-ash berries (*Sorbus*), when it passes over together with water as a yellow fragrant oil, which becomes a crystalline solid when boiled for some time with strong HCl, or when fused with KHO and precipitated by an acid.

Sorbic acid fuses at 134°.5 C., and is decomposed when distilled, unless in presence of steam. It is sparingly soluble in water, but dissolves in alcohol.

Palmitolic acid, $C_{15}H_{27}.CO_2H$, is of no practical importance. It is a crystalline solid, insoluble in water, and fusing at 42° C. Nitric acid oxidises it to suberic acid, $C_6H_{12}(CO_2H)_2$.

Stearolic acid, $C_{17}H_{31}.CO_2H$, another acid of little importance, forms crystals sparingly soluble in cold alcohol, fusing at 48° C., and subliming undecomposed. Nitric acid converts it, eventually, into azelaic acid, $C_7H_{14}(CO_2H)_2$, the next homologue of suberic acid.

Behenolic acid, $C_{21}H_{39}.CO_2H$, is also crystalline, and fuses at 57°.5 C.

373. *General remarks on the sorbic series of acids.* These may be obtained from the acids of the oleic series, by combining them with two atoms of bromine and treating the product with alcoholic solution of potash (see above). These acids also combine with two and four atoms of bromine, and are converted by nitric acid into new acids by taking up two atoms of oxygen.

Thus we have the acids—

$C_5H_7Br_2.CO_2H$	formed on the	type of	pyroterebic	acid,	$C_5H_9.CO_2H$
$C_5H_7Br_4.CO_2H$	,,	,,	caproic	,,	$C_5H_{11}.CO_2H$
$C_{15}H_{29}Br_2.CO_2H$ $C_{15}H_{27}O_2.CO_2H$ (*palmitoxylic acid*)	,,	,,	palmitic	,,	$C_{15}H_{31}.CO_2H$
$C_{17}H_{31}Br_2.CO_2H$	,,	,,	oleic	,,	$C_{17}H_{33}.CO_2H$
$C_{17}H_{31}Br_4.CO_2H$ $C_{17}H_{31}O_2.CO_2H$ (*stearoxylic acid*)	,,	,,	stearic	,,	$C_{17}H_{35}.CO_2H$
$C_{21}H_{39}O_2.CO_2H$ (*behenoxylic acid*)	,,	,,	behenic	,,	$C_{21}H_{43}.CO_2H$

374. *Benzoic* or *phenyl-formic acid*, $C_6H_5.CO_2H$, is prepared from naphthalene, $C_{10}H_8$; this is first converted into naphthalene tetrachloride, $C_{10}H_8Cl_4$, by the action of chlorine, or of potassium chlorate and hydrochloric acid; the naphthalene tetrachloride is boiled with nitric acid, which converts it into phthalic acid, $C_6H_4(CO_2H)_2$; this is neutralised with lime, and the dried calcium phthalate is heated with slaked

lime to between 300° and 350° C. for some hours, when it becomes converted into calcium benzoate—

$$2C_6H_4(CO_2)_2Ca + Ca(OH)_2 = (C_6H_5CO_2)_2Ca + 2CaCO_3.$$

The calcium benzoate is decomposed by HCl, when the benzoic acid is precipitated in crystals.

Benzoic acid is also made from toluene, $C_6H_5.CH_3$; when Cl is passed into boiling toluene, it produces benzyl chloride, $C_6H_5.CH_2Cl$, which may be converted into benzoic acid by oxidising it with nitric acid.

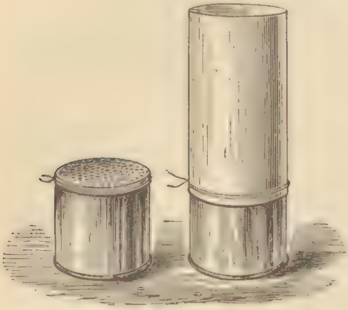

Fig. 279.

Benzoic acid was originally extracted from *gum benzoin*, a resinous exudation from *Styrax benzoin*, a tree of the Malay Islands. When the gum is gently heated in an iron or earthen vessel, covered with perforated paper and surmounted by a drum of paper (fig. 279), the benzoic acid rises in vapour and condenses in the drum. A better yield is obtained by boiling the benzoin with lime and water, and decomposing the filtered solution of calcium benzoate with hydrochloric acid.

Benzene, C_6H_6, may be partly converted into benzoic acid by oxidising it with MnO_2 and H_2SO_4. Addition of formic acid increases the yield of benzoic acid; $C_6H_6 + H.CO_2H + O = C_6H_5.CO_2H + H_2O$.

Another source of benzoic acid is the urine of cows and horses, which contains hippuric acid, easily convertible into benzoic (see *Hippuric acid*).

Benzoic acid occurs among the products of oxidation of albuminous compounds with MnO_2 and H_2SO_4.

Properties of benzoic acid.—It crystallises in shining needles or in feathery scales, usually having a faint aromatic odour. It fuses at 120° C. and boils at 250°, subliming without decomposition; it volatilises when boiled with water. It is sparingly soluble in cold water (200 parts), more easily in hot water (24 parts); alcohol and ether dissolve it readily. Potash and ammonia also dissolve it immediately, and it is reprecipitated on adding an acid. Most of the benzoates are soluble, but *ferric benzoate* is obtained as a buff-coloured precipitate when ferric chloride is added to a neutral benzoate.

By distillation with excess of lime, benzoic acid yields benzene—

$$C_6H_5.CO_2H + CaO = CaCO_3 + C_6H_6.$$

When vapour of benzoic acid is passed over heated zinc-dust, it is converted into bitter-almond oil (benzoic aldehyd)—

$$C_6H_5.CO_2H + Zn = C_6H_5.COH + ZnO.$$

By boiling with strong HNO_3, benzoic acid is converted into nitrobenzoic acid, $C_6H_4NO_2.CO_2H$.

By distilling benzoic acid with PCl_3, *benzoyl chloride* is obtained; $C_6H_5.CO.OH + PCl_3 = C_6H_5.COCl + PClO + HCl$. This chloride bears the same relation to benzoic acid as acetyl chloride bears to acetic acid, the radicals benzoyl and acetyl being related in a similar way to benzyl and ethyl;

Ethyl, C_2H_5; Acetyl, C_2H_3O''	Benzyl, C_7H_7; Benzoyl, C_7H_5O''
Ethyl hydride (ethane), C_2H_6	Benzyl hydride (toluene), C_7H_8
Ethyl hydrate (alcohol), $C_2H_5.HO$	Benzyl hydrate, $C_7H_7.HO$
Acetyl hydride (aldehyd), C_2H_4O	Benzoyl hydride, C_7H_6O
Acetyl hydrate (acetic acid), $C_2H_4O_2$	Benzoyl hydrate, $C_7H_6O_2$

375. *Benzoic anhydride*, or *dibenzoyl oxide*, $(C_6H_5.CO)_2O$, is produced by heating benzoyl chloride with dry sodium benzoate—

$$C_6H_5.COCl + C_6H_5.CO.ONa = (C_6H_5CO)_2O + NaCl.$$

The mass is washed with water and the anhydride crystallised from alcohol. It fuses at 42° C. and boils at 310°. Boiling with water converts it slowly into benzoic acid.

By heating benzoyl chloride with dry sodium acetate, the *benzoacetic anhydride* is obtained; $C_6H_5.COCl + CH_3.COONa = (C_6H_5CO)(CH_3CO)O + NaCl$.

Benzoic peroxide, $(C_6H_5CO)_2O_2$, is obtained by acting on benzoyl chloride with barium dioxide; $2C_6H_5COCl + BaO_2 = (C_6H_5CO)_2O_2 + BaCl_2$. It may be crystallised from ether. Like hydric peroxide, it is decomposed explosively when moderately heated. Alkalies resolve it into benzoic acid and oxygen.

376. *Toluic acid*, or *methyl-benzoic acid*, $C_6H_4.CH_3.CO_2H$, is obtained by oxidising xylene, $C_6H_4(CH_3)_2$, with dilute nitric acid. It crystallises in needles fusing at 102° C., and is sparingly soluble in water.

Mesitylenic acid, $C_8H_9.CO_2H$, is prepared by oxidising mesitylene, $C_6H_3(CH_3)_3$, with dilute nitric acid. It is a crystalline volatile acid, fusing at 166° C., soluble in boiling water and in alcohol. *Mesitylene* is a product of the dehydrating action of sulphuric acid on acetone; $3(CH_3.CO.CH_3) = C_6H_3(CH_3)_3 + 3H_2O$.

Cuminic or *propyl-benzoic acid*, $C_6H_4(C_3H_7).CO_2H$, is prepared from the aldehyd existing in Roman cummin oil, by boiling it with alcoholic solution of potash, which converts it into cuminic alcohol and potassium cuminate—

$$2C_6H_4(C_3H_7)COH + KOH = C_7H_6(C_3H_7)OH + C_6H_4(C_3H_7)CO_2K.$$

On adding an acid to the aqueous solution of potassium cuminate, the cuminic acid is precipitated, and may be crystallised from alcohol; it fuses at 114° C., and may be sublimed.

Durylic or *trimethyl-benzoic acid*, $C_6H_2(CH_3)_3.CO_2H$, metameric with cuminic acid, is formed when durene, $C_6H_2(CH_3)_4$, is oxidised with dilute nitric acid; it fuses at 149° C.

Homocuminic acid, the next homologue, $C_6H_4.CH_2(C_3H_7)CO_2H$, is of no practical importance.

377. *General remarks on the benzoic or aromatic series of acids.*—These acids are crystalline, volatile, sparingly soluble in water, but soluble in alcohol and ether. When distilled with excess of lime, they yield hydrocarbons of the benzene series, CO_2 being abstracted.

378. *Cinnamic* or *phenyl-acrylic acid*, $C_2H_2.C_6H_5.CO_2H$, is prepared by boiling storax with soda, and decomposing the solution of sodium cinnamate with HCl, which precipitates the cinnamic acid in feathery crystals like benzoic acid, fusing at 133° C., boiling at 290°, and subliming undecomposed. It is soluble in boiling water and in alcohol.

Its connexion with acrylic acid is shown by fusing it with potash, which yields acetate and benzoate of potassium, whilst acrylic acid yields acetate and formate; $C_2H_2.C_6H_5.CO_2H + 2KOH = CH_3.CO_2K + C_6H_5.CO_2K + H_2$.

Oxidising agents convert cinnamic acid into benzoic aldehyd (bitter-almond oil); $C_2H_2.C_6H_5.CO_2H + O_4 = C_6H_5.COH + 2CO_2 + H_2O$. When distilled with excess of lime, it yields *cinnamene* or *phenyl-ethylene*—

$$C_2H_2.C_6H_5.CO_2H + CaO = C_2H_3.C_6H_5 + CaCO_3.$$

Nascent hydrogen converts it into phenyl-propylic acid—

$$C_2H_2.C_6H_5.CO_2H + H_2 = C_2H_4.C_6H_5.CO_2H.$$

Cinnamic acid may be obtained synthetically by the action of sodium acetate on bitter-almond oil, in presence of acetic anhydride, which probably acts as a dehydrating agent; $CH_3CO_2Na + C_6H_5COH = C_2H_2.C_6H_5.CO_2Na + H_2O$.

Atropic acid, isomeric with cinnamic, is produced when atropine, the alkaloid of deadly nightshade, is boiled with baryta or with HCl. It is crystalline, and fuses at 106° C.

The other members of the cinnamic series are of no practical importance. They may be prepared from benzoic aldehyd or cuminic aldehyd, as cinnamic acid is, by treatment with the anhydrides and sodium salts of members of the acetic series.

379. *Glycolic* or *hydroxyacetic acid*, $CH_2.HO.CO_2H$, is prepared by the careful oxidation of alcohol by nitric acid. Into a narrow glass cylinder (2 inches in diameter) pour 118 cubic centimetres of 80 per cent. alcohol; insert a funnel tube drawn out to a fine opening, to the bottom of the vessel, and pour in 50 c.c. of water, so as to form a layer below the alcohol; then pour in carefully through the funnel 126 c.c. of nitric acid, of sp. gr. 1.35, to form a layer below the water. Place the vessel aside, without shaking, for about five days at about 20° C., when the three layers will have mixed. Evaporate the liquid upon the water-bath, in separate portions of about 20 c.c., to a syrup, dilute it with 10 volumes of water, boil, and neutralise with powdered chalk. To the crystalline paste which forms on cooling add an equal bulk of alcohol, and filter. The precipitate is boiled with water, and filtered, while boiling, from undissolved calcium oxalate. On cooling, it deposits calcium glyoxalate, whilst calcium glycolate remains in solution; this is boiled with a little lime to decompose any glyoxalate, and the filtered solution evaporated and treated with enough oxalic acid to precipitate the calcium as oxalate, leaving glycolic acid in solution.

The action of nitric acid upon alcohol is of a representative character. Ethyl-alcohol, $C_2H_5.OH$, is derived from methyl-alcohol, $CH_3.OH$, by the substitution of the methyl-group CH_3 for H, so that ethyl-alcohol should be written $CH_2.CH_3.OH$, or $CH_3.CH_2.OH$. Now, the groups CH_3 and $CH_2.OH$, under the influence of oxidising agents, are converted into CHO'', characteristic of the aldehyds, and $CO.OH$, characteristic of the acids. Accordingly, we find, among the products of the above operation, acetic aldehyd, $CH_3.CHO$; acetic acid, $CH_3.CO.OH$; glyoxal, $CHO.CHO$; glyoxylic acid, $CHO.CO.OH$; glycolic acid, $CH_2.HO.CO.OH$; and oxalic acid, $CO.OH.CO.OH$.

Glycolic acid has been obtained by allowing the vinegar ferment, *bacterium aceti*, to grow in a dilute solution of glycol (ethene-alcohol).

Properties of glycolic acid.—Crystallises with some difficulty; fuses at 80° C. and volatilises slowly at 100°. Very soluble in water, alcohol, and ether. As might be expected, oxidising agents convert it into oxalic acid. When heated with sulphuric acid, it yields formic aldehyd and formic acid; $CH_2.HO.CO_2H = HCHO + HCO_2H$. The formic aldehyd is converted into formic paraldehyd, $(HCHO)_3$, and most of the formic acid is decomposed into H_2O and CO.

When glycolic acid is heated with HCl, it yields chloracetic acid; $CH_2.HO.CO_2H + HCl = CH_2.Cl.CO_2H + H_2O$. This acid may be reconverted into glycolic by boiling with KHO, which replaces the Cl by HO.

Hydriodic acid reduces glycolic to acetic acid—

$$CH_2.HO.CO_2H + 2HI = CH_3.CO_2H + H_2O + I_2.$$

The glycolates of calcium, copper, and silver are sparingly soluble in cold water, but dissolve in boiling water.

Glycolic acid occurs in unripe grapes, and in the leaves of the Virginia creeper. It can be made from glucose by oxidising it with silver oxide, in the presence of calcium carbonate to keep the solution neutral, or else the glycolic acid becomes oxalic acid.

380. *Lactic acid*, $C_2H_5O.CO_2H$, or *hydroxypropylic acid*—

$$C_2H_4.HO.CO_2H,$$

is prepared by fermenting glucose with putrid cheese, in presence of chalk, as described at p. 513, and decomposing the calcium lactate with dilute sulphuric acid, not in excess. The solution of lactic acid is filtered from the $CaSO_4$, and purified by neutralising with zinc carbonate, recrystallising the zinc lactate, and precipitating the zinc by H_2S, when lactic acid is obtained in solution. When this is evaporated, it leaves a syrupy liquid containing lactic acid, water, and *lactic anhydride*, $(C_3H_5O_2)_2O$. On attempting to expel all the water, a crystalline body, *lactide*, is produced; $2(C_2H_5O.CO_2H) = C_6H_8O_4 + 2H_2O$. Perfectly pure lactic acid has not been obtained.

The acid prepared in this way is known as ordinary or *fermentation* lactic acid; it is found in sour milk, being produced by the fermentation of the milk-sugar, and in small quantity in the gastric juice, and in opium.

Lactic acid is a strongly acid liquid which does not distil without decomposition, when one part is converted into lactide and another into aldehyd, CO and H_2O; $C_2H_5O.CO_2H = CH_3.CHO + CO + H_2O$. If the pressure be diminished, much of the acid may be distilled.

When lactic acid is heated to 130° C. with dilute sulphuric acid, in a sealed tube, it yields aldehyd and formic acid—

$$C_2H_5O.CO_2H = CH_3.COH + H.CO_2H.$$

With strong sulphuric acid, the formic acid is converted into water and CO. Nitric acid oxidises lactic acid to oxalic acid. Chromic acid converts it into acetic acid, CO_2 and H_2O—

$$C_2H_5O.CO_2H + O_2 = CH_3.CO_2H + CO_2 + H_2O.$$

Since lactic acid is hydroxypropylic, it may be reduced to propylic acid by strong hydriodic acid—

$$C_2H_4.HO.CO_2H + 2HI = C_2H_5.CO_2H + H_2O + I_2.$$

Conversely, propylic acid may be converted into lactic by the following steps:—

$$(1)\ C_2H_5.CO_2H + Br_2 = C_2H_4.Br.CO_2H + HBr;$$
$$(2)\ C_2H_4Br.CO_2H + KHO = C_2H_4.HO.CO_2H + KBr.$$

Lactic acid is producible from aldehyd by heating it with a strong solution of hydrocyanic acid, treating the product with strong HCl, and afterwards boiling with water; $CH_3.CHO + CHN + HCl + 2H_2O = CH_3.CH_2O.CO_2H + NH_4Cl$; the intermediate stages are omitted.

The *lactates* are mostly soluble; the most important of them is the *zinc lactate*, $(C_2H_5O.CO_2)_2Zn.3H_2O$, which is sparingly soluble in water, and is precipitated in prismatic crystals when zinc sulphate is added to lactic acid neutralised by ammonia.

Paralactic or *sarcolactic acid* is isomeric with lactic acid, and is found in the juice of flesh, in bile, and in urine of persons poisoned by phosphorus. It differs from lactic acid in its optical property of rotating the plane of polarisation to the right, whereas lactic acid is optically inactive. But if the sarcolactic acid be kept in a desiccator for some time, it becomes converted into anhydrides (corresponding to lactide), the solution of which produces a strong rotation to the left. When sarcolactic acid is heated to obtain the anhydrides, they yield inactive lactic acid when dissolved. The *zinc sarcolactate* contains only $2H_2O$, and is about three times as soluble in water as the lactate.

Ethylene lactic acid, also found in juice of flesh, forms an amorphous zinc salt, and yields oxalic and carbonic acids, instead of acetic, when oxidised by chromic acid.

381. *Butylactic acid*, or *hydroxybutyric acid*, $C_3H_6.HO.CO_2H$, is formed by heating butyric acid with bromine, and decomposing the bromobutyric acid then produced with moist silver oxide; (1) $C_3H_7.CO_2H + Br_2 = C_3H_6Br.CO_2H + HBr$;

(2) $2(C_3H_6Br.CO_2H) + H_2O + Ag_2O = 2AgBr + 2(C_3H_6(HO).CO_2H)$. It is a liquid, boiling at 217° C., but not distilling without decomposition.

Valerolactic or *hydroxyvaleric acid*, $C_4H_8(HO).CO_2H$, is obtained in a similar way from valeric acid. It is a crystalline solid, fusing at 80° C. and subliming below 100°. It dissolves in water, alcohol, and ether, and is oxidised by CrO_3 to (iso)butyric and carbonic acids.

Leucic or *hydroxycaproic acid*, $C_5H_{10}(HO).CO_2H$, is prepared by the action of nitrous acid on *leucine*, or *amido-isocaproic acid*, $C_5H_{10}(NH_2).CO_2H$, a crystalline substance found in bullocks' lungs, and formed in the decomposition of many animal products; $C_5H_{10}(NH_2).CO_2H + HNO_2 = H_2O + N_2 + C_5H_{10}(HO).CO_2H$. Leucic acid crystallises in needles which fuse at 73° C. and sublime below 100°. Its salts are sparingly soluble.

382. It will have been noticed that the acids of the lactic series may be obtained from those of the acetic series by converting these into chloro- or bromo-substitution products, and afterwards replacing the Cl or Br by HO, by treatment with potash or moist silver oxide. The presence of the HO group in these acids causes them to behave in some respects as alcohols as well as acids, the H of the HO group admitting of replacement by metals and alcohol radicals, as well as the H of the CO_2H group. Hence they are sometimes referred to as *alcohol acids* or *monobasic diatomic acids*. Thus, if lactic acid be neutralised with soda or sodium carbonate, it behaves like a monobasic acid, yielding sodium lactate, $C_2H_4.HO.CO_2Na$, and if this be heated with sodium, H is evolved, and *sodio-lactate of sodium*, $C_2H_4.NaO.CO_2Na$, is produced. When treated with water, this is decomposed, sodium lactate and hydrate being formed.

383. *Salicylic* or *hydroxybenzoic acid*, $C_6H_4.HO.CO_2H$, is prepared artificially by combining phenol with soda, and heating the product in carbonic acid gas. The phenol, with half its weight of NaHO, is dissolved in a little water and evaporated to dryness. The sodium phenol is powdered, placed in a flask or retort, which is heated to 100° C. in a slow stream of dry CO_2 for some hours. The temperature is then raised to 180° C., when phenol distils over, and continues to do so till the temperature has risen to 250° C. The residue is dissolved in a small quantity of water, and strong HCl added to precipitate the salicylic acid, which may be purified by crystallisation from water.

By dissolving phenol in soda, sodium-phenol is produced—

$$C_6H_5.OH + NaOH = C_6H_5.ONa + HOH.$$

When this is heated in CO_2, it yields phenol and sodio-salicylate of sodium; $2C_6H_5.ONa + CO_2 = C_6H_5.OH + C_6H_4.NaO.CO_2Na$; this last, decomposed by HCl, yields salicylic acid—

$$C_6H_4.NaO.CO_2Na + 2HCl = C_6H_4.HO.CO_2H + 2NaCl.$$

Salicylic acid was formerly made from *oil of winter-green* (*Gaultheria*, a North American plant of the Heath order), which is the *methyl salicylate*, $C_6H_4.HO.CO_2.CH_3$. Its original source was salicin, a glucoside extracted from willow-bark, which yields the salicylate when fused with potash. Salicylic acid has been found in the leaves, stems, and rhizomes of some of the *Violaceæ*, and in the garden pansy.

Properties of salicylic acid.—It forms four-sided prisms which fuse at 156° C., and sublime if carefully heated; but a temperature of 220° decomposes it into phenol and CO_2; $C_6H_4.HO.CO_2H = CO_2 + C_6H_5.OH$. It dissolves sparingly in cold water, more easily on heating, and is soluble in alcohol and ether. Its solution gives an intense violet colour with ferric chloride. It possesses antiseptic properties, and is used for the preservation of articles of food, being free from taste and smell.

The salicylates of K and Na are crystallisable; barium salicylate, $(C_6H_4.HO.CO_2)_2Ba.Aq$, also crystallises, and, when boiled with baryta-water, yields a sparingly soluble salt, $C_6H_4BaOCO_2.2Aq$, in which the diad Ba replaces the H of the hydroxyl as well as that of the carboxyl, showing that salicylic acid is an alcohol-acid like the members of the lactic series.

Anisic acid, or *methyl-(para)oxybenzoic acid*, $C_6H_4.CH_3O.CO_2H$, is metameric with the oil of winter-green, and is formed by the oxidation of its aldehyd, which occurs in oil of anise (p. 505). It may be formed artificially from salicylic acid by heating its potassium salt to 220°, when it yields dibasic potassium paraoxybenzoate, which is converted into potassium anisate when treated successively with methyl iodide and caustic potash; $2(C_6H_4.HO.CO_2K)$ (*potassium salicylate*) = $C_6H_5.OH$ (*phenol*) + CO_2 + $C_6H_4.KO.CO_2K$ (*dibasic potassium para-oxybenzoate*);

$C_6H_4.KO.CO_2K + 2CH_3I = C_6H_4.CH_3.O.CO_2.CH_3$ (*methyl anisate*) + 2KI;

$C_6H_4.CH_3O.CO_2.CH_3 + KOH = C_6H_4.CH_3O.CO_2K$ (*potassium anisate*) + $CH_3.OH$.

Hydrochloric acid precipitates the anisic acid, which may be dissolved in alcohol and crystallised. It forms prisms fusing at 175° C. and subliming undecomposed.

384. *Protocatechuic* or *dihydroxybenzoic acid*, $C_6H_3(HO)_2.CO_2H$, is prepared by the action of fused caustic soda on *kino*, a gum-resin exuding from certain Indian and African leguminous plants, and employed in medicine as an astringent. One part of powdered kino is added to three parts of fused caustic soda, and the heat continued till the mass has a pale orange-brown colour. It is then cooled, dissolved in twenty parts of water, the solution acidulated with H_2SO_4, allowed to stand, and filtered. The filtered liquid is shaken with ether, the ethereal layer drawn off and distilled, when the protocatechuic acid is left in the retort. It crystallises in plates or needles containing H_2O, which fuse at 199° C., and are soluble in water, alcohol, and ether. Ferric chloride gives a green colour with the acid, which is changed to blue and red by alkalies. When heated, it is decomposed, yielding *pyrocatechin*: $C_6H_3(HO)_2.CO_2H - CO_2 + C_6H_4(HO)_2$.

Protocatechuic acid is a very common product of the action of fused potash or soda on the large class of bodies known as *gum-resins*, and acquired its name from its production in this way from *catechu* (*Cutch* or *Terra japonica*), a substance much used in dyeing black, extracted by boiling water from the inner bark wood of the *Mimosa catechu* of the East Indies.

It will be found that the formation of this acid during the *potash-fusion* of an organic substance often throws light upon its constitution.

Phloretic acid, $C_6H_3.CH_3.OCH_3.CO_2H$, or $C_9H_{10}O_3$, homologous with salicylic acid, $C_7H_6O_3$, and anisic acid, $C_8H_8O_3$, is formed by the action of potash on phloretin, a product of the hydrolysis of the glucoside phlorizin, obtained from fruit trees—

$$\underset{\textit{Phloretin.}}{C_{15}H_{14}O_5} + KHO = \underset{\textit{Potassium phloretate.}}{C_8H_9O.CO_2K} + \underset{\textit{Phloroglucol.}}{C_6H_3(OH)_3}$$

Phloretic acid crystallises in prisms which are soluble in hot water, alcohol, and ether. Ferric chloride colours its solution green. When distilled with lime, it yields *phlorol*, $C_6H_4.CH_2(CH_3).OH$.

Vanillic or *methyl-protocatechuic acid*, $C_6H_3.HO.CH_3O.CO_2H$, is produced when vanillic aldehyd (vanillin) is exposed to moist air. It may also be made by oxidising the glucoside coniferin with potassium permanganate. It crystallises in plates, fusing at 211° C. and subliming unchanged. When heated in a sealed tube with dilute HCl to 160° C., it yields protocatechuic acid and methyl chloride; $C_6H_3.HO.CH_3O.CO_2H + HCl = C_6H_3(HO)_2.CO_2H + CH_3Cl$. Vanillic acid is metameric with anisic acid.

385. *Tannic acid*, or *tannin*, $C_{13}H_9O_7.CO_2H$, is extracted by water from gall-nuts, ether being used at the same time to dissolve the colouring matter and gallic acid. 240 grammes of powdered gall-nuts are digested for some hours, with frequent shaking, with 1800 cubic centimetres of ether and 150 of water. The mixture is poured into a funnel loosely plugged with cotton, and the filtered liquid allowed to stand, when it separates into two layers, the upper one being the ethereal solution of colouring matter, &c., and the lower an aqueous solution of tannic acid, which is evaporated to dryness at a low temperature.

Tannic acid does not crystallise, but is left, on evaporation, in brownish-white shining scales, which are very easily soluble in water, but sparingly in alcohol and in anhydrous ether. Its solution is astringent, feebly acid, and gives a bluish-black precipitate with ferric chloride. H_2SO_4 and HCl combine with it to form white precipitates, and a solution of gelatin precipitates a very insoluble compound with tannic acid. Albumen, starch, and most of the alkaloids are also precipitated by tannic acid. Common salt causes the separation of tannic acid from its solution. Lead acetate precipitates it as basic tannate, which is insoluble in acetic acid. Copper sulphate also precipitates it immediately. Alum and potash added to tannic acid give a precipitate insoluble in cold potash. Potash or ammonia added to a solution of tannic acid renders it brown, especially if shaken with air, absorption of oxygen taking place. Tannic acid acts as a reducing agent upon alkaline cupric solutions, producing cuprous oxide. It is decomposed by distillation, one of the products being *pyrogallol*, $C_6H_3(OH)_3$.

Alcoholic solutions of tannic acid and potash yield a precipitate of *potassium tannate*, $C_{13}H_9O_7.CO_2K$, and if this be dissolved in water, and $BaCl_2$ added, *barium tannate*, $(C_{13}H_9O_7.CO_2)_2Ba$, is precipitated.

Tannic acid may be extracted from *sumach*, the ground shoots of the *Rhus coriaria*, a tropical plant of the Cashew order. It is also contained in oak-bark.

The properties above described are those of *gallo-tannic* or *quercitannic* acid. Many other plants yield substances resembling this in astringency, in giving nearly black precipitates with ferric salts, and in forming insoluble compounds with gelatin, but differing slightly in some of their properties. Thus we have tannic acids from cinchona-bark (*quino-tannic*), from coffee (*caffeo-tannic*), from catechu, and from fustic (mori-tannic acid), a yellow dye-wood from a tree of the mulberry order (*Morus tinctoria*). These give dark *green* precipitates with ferric salts, and, when distilled, yield pyrocatechin, $C_6H_4(OH)_2$, instead of pyrogallin, $C_6H_3(OH)_3$. All the varieties are important from their applications in the tanning of skins, in dyeing, and in the manufacture of ink. Some of them are valuable medicines.

Gallic or *trihydroxybenzoic acid*, $C_6H_2(HO)_3.CO_2H$, is prepared by keeping moistened powdered gall-nuts for some weeks in a warm place, so that they may undergo fermentation, and extracting the gallic acid by boiling with water, from which it crystallises in fine needles containing H_2O. The gallic acid is formed by the decomposition of the tannic acid of the galls. Gallic acid may also be prepared by boiling tannic acid with dilute sulphuric acid—

$$C_{13}H_9O_7.CO_2H + H_2O = 2C_6H_2(HO)_3CO_2H.$$

Gallic acid differs greatly from tannic in crystallising very readily from an aqueous solution; it dissolves in 3 parts of boiling water and in 100 of cold water. Alcohol and ether dissolve it more easily than tannic acid. It loses its water at 100° C. and fuses at 200°. A temperature of 220° decomposes it, yielding a crystalline sublimate of pyrogallol; $C_6H_2(HO)_3.CO_2H = C_6H_3(HO)_3 + CO_2$. Solution of gallic acid is not precipitated by H_2SO_4 or HCl, or by gelatin. Lead acetate precipitates it, but the precipitate is soluble in acetic acid. Alum and potash give a precipitate easily soluble in potash. Ferric salts give a bluish-black precipitate, and the alkalies give a brown-red colour, especially on exposure to air, a compound called *tanno-melanic acid*, $C_6H_4O_3$, being produced, which is also formed by the action of nitrous acid on gallic acid. Gallic acid is found in several vegetable products, some of which are used in dyeing and tanning; as in *divi-divi*, the fruit of a leguminous plant, *Cæsalpinia coriaria*, in sumach, in mangoes, and the leaves of the wild vine, a tropical plant of the Moon-seed order (*Cissampelos pareira*), useful in medicine.

The salts of gallic acid are not well known; *potassium gallate*, $C_6H_2(HO)_3.CO_2K$, may be obtained artificially by heating di-iodosalicylic acid with solution of potassium carbonate to 140° C. in a sealed tube—

$$C_6H_2I_2(HO).CO_2H + K_2CO_3 + H_2O = C_6H_2(HO)_3.CO_2H + 2KI + CO_2.$$

When gallic acid is heated with 4 parts of strong H_2SO_4 to 75° C., it gives a dark red solution, and if this be cooled and poured into water, a red precipitate is obtained which has the composition $C_{14}H_8O_8.2Aq$, or twice gallic acid, minus $2H_2O$. This was formerly termed *rufigallic acid*, but is really *hexa-hydroxyanthraquinone*, $C_{14}H_2(HO)_6O_2$, for zinc-dust reduces it to anthracene, $C_{14}H_{10}$.

When gallic acid is heated with PCl_3O to 120° C. for some hours, it loses H_2O and becomes *digallic acid*; $2C_6H_2(OH)_3CO_2H = (C_6H_2(OH)_3CO)_2O + H_2O$. This body, which should rather be termed *gallic anhydride*, very nearly resembles tannic acid, and is believed by some to be identical with it, being an amorphous substance, soluble in water, strongly astringent, and giving a dark blue precipitate with ferric salts. It is converted into gallic acid by boiling with HCl. Gallic acid is also converted into digallic by boiling its alcoholic solution with arsenic acid.

Ellagic acid, $C_{13}H_9O_8.CO_2H$, is obtained by oxidising gallic or tannic acid with arsenic anhydride; it is a yellowish crystalline powder sparingly soluble in water and alcohol. It is found in *bezoar-stones*, the calculi sometimes formed in the intestines of wild goats in Persia.

Caffeic acid, $C_8H_7O_2.CO_2H$, is obtained by boiling with caustic potash the residue left on evaporating the aqueous decoction of coffee, and precipitating the solution by HCl. It crystallises out in plates on cooling, and is soluble in alcohol. It yields pyrocatechin when heated, and is converted into acetate and protocatechuate when fused with potash—

$$C_8H_7O_2.CO_2H + 2KHO = CH_3.CO_2K + C_6H_3(OH)_2.CO_2K + H_2.$$

Quinic or *kinic acid*, $C_6H_7(OH)_4.CO_2H$, is found in cinchona bark, in coffee and some other plants. It is crystalline and soluble. Like caffeic acid, it gives pyrocatechin when distilled, and protocatechuic acid when fused with potash. When heated with manganese dioxide and sulphuric acid, it is oxidised to quinone, which sublimes in yellow needles—

$$C_6H_7(OH)_4.CO_2H + O_2 = C_6H_4O_2\ (\textit{quinone}) + CO_2 + 4H_2O.$$

386. *Saccharic acid*, $C_4H_8O_4(CO_2H)_2$, is obtained by oxidising sugar or starch with nitric acid, stopping short of the formation of oxalic acid. Sugar is heated with 3 parts of nitric acid of sp. gr. 1.3, till violent action begins. When no more red fumes are evolved, it is kept at 50° C. for some hours, diluted with two or three volumes of water, neutralised with K_2CO_3, and acidified strongly with acetic acid. On standing, *hydropotassium saccharate*, $C_4H_8O_4(CO_2)_2HK$, crystallises out. This is dissolved in a little potash, and precipitated by cadmium chloride. The precipitate of cadmium saccharate is suspended in water and decomposed by H_2S, the CdS filtered off, and the solution of saccharic acid evaporated. Saccharic acid forms a deliquescent amorphous mass, soluble in alcohol and in water. Its salts are somewhat similar to those of tartaric acid, $C_2H_4O_2(CO_2H)_2$, the acid salts of potassium and ammonium being sparingly soluble. *Calcium saccharate*, $C_4H_8O_4(CO_2)_2Ca.Aq$, is crystalline, nearly insoluble in water, but soluble in acetic acid.

Mucic acid, $C_4H_8O_4(CO_2H)_2$, isomeric with saccharic, is prepared by oxidising gum arabic or milk sugar with nitric acid. Milk sugar is heated with 3 parts of nitric acid of sp. gr. 1.3 until red fumes are abundant; the heat is then removed, when the acid separates as a granular powder sparingly soluble in water and alcohol. The macates differ greatly from the saccharates, most of them being insoluble; the acid potassium salt is more soluble than the normal salt. By boiling mucic acid with water for some time, it is converted into *paramucic acid*, which is isomeric with it, but more soluble in alcohol. Hydriodic acid reduces saccharic and mucic acids to *adipic acid*—

$$C_4H_8O_4(CO_2H)_2 + 8HI = C_4H_8(CO_2H)_2 + 4H_2O + 4I_2.$$

Pyromucic acid, $C_4H_3O.CO_2H$, is a product of the distillation of mucic acid, and may also be obtained by boiling furfurol (pyromucic aldehyd, page 506) with silver oxide and water. It forms prismatic crystals sparingly soluble in cold water, soluble in hot water, alcohol, and ether. It may be sublimed. The pyromucates are very soluble.

387. *Oxalic acid*, $(CO_2H)_2$, is prepared on the small scale by oxidising sugar with nitric acid, and on the large scale by oxidising sawdust with potash.

Preparation of oxalic acid from sugar.—50 grms. of sugar are gently heated in a flask with 250 c.c. of ordinary concentrated nitric acid, sp. gr. 1.4. When the action commences, remove the heat, when the oxidation will continue violently. On cooling, part of the oxalic acid will crystallise out, and more will be obtained by concentrating the mother-liquor. Drain the crystals on a funnel, and dissolve them in as little boiling water as possible, so as to purify the acid by recrystallisation. It may be allowed to dry by exposure to air.

Preparation of oxalic acid from sawdust.—Common pine sawdust is made into a thick paste with a solution containing $KHO + 2NaHO$ of sp. gr. 1.35. This is spread on iron plates, dried up, and heated just short of carbonisation. The cellulose, $C_6H_{10}O_5$, is thus oxidised, with evolution of hydrogen, and converted into oxalic acid, which remains in the mass as oxalates of potassium and sodium. These are dissolved in water, and boiled with lime, which produces the insoluble calcium oxalate, together with solution of the caustic alkalies, which may be used again. The calcium oxalate is decomposed by dilute sulphuric acid, the solution of oxalic acid filtered from the calcium sulphate and crystallised.

Strictly speaking, in carrying out this process, the fused mass is treated with a small quantity of hot water, which leaves the bulk of the sodium oxalate undissolved; this is decomposed by lime, as stated above. The liquor, which contains but little oxalate, is boiled to dryness, the residue heated, and the alkaline carbonate caustified by lime. It is worth noting that caustic soda alone would produce very little oxalate. When potash is cheap, it may be used alone.

Oxalic acid occurs in sorrel, rhubarb, and many other plants. Potassium oxalate is formed when potassium formate is gently heated; $2(H.CO.OK) = H_2 + (CO_2K)_2$. Sodium oxalate is produced when sodium, mixed with sand to moderate the action, is heated to 360° C. in dry CO_2; $Na_2 + 2CO_2 = (CO_2Na)_2$.

Properties of oxalic acid.—It forms monoclinic prisms containing 2Aq, which are soluble in nine parts of cold water and in alcohol. It is a very strong acid, able to decompose the nitrates and chlorides. In large doses it is poisonous. When gently heated, the crystals effloresce from loss of water, and begin to vaporise slowly at 100° C. Heated to 165°, it sublimes freely, part being decomposed into formic acid and CO_2; $(CO_2H)_2 = H.CO_2H + CO_2$. A weak solution of oxalic acid is decomposed by boiling. When heated with strong sulphuric acid, $(CO_2H)_2 = CO_2 + CO + H_2O$, the CO burning on applying a flame. If oxalic acid be dissolved in twelve parts of warm oil of vitriol, and set aside, large rhombic octahedra of $(CO_2H)_2$ are deposited. Oxalic acid is largely used in dyeing, calico-printing, and bleaching, in cleaning brass, and in removing iron-mould from linen. It is a dibasic acid.

Normal *potassium oxalate*, $(CO_2K)_2.Aq$, is moderately soluble in water.

Hydropotassium oxalate, or *potassium binoxalate*, or *salt of sorrel*, is

$(CO_2)_2KH$. It is also called *essential salt of lemons*, though lemons contain no oxalic acid.

Hydropotassic oxalate requires 40 parts of cold water to dissolve it, and has occasionally caused accidents by being mistaken for cream of tartar, hydropotassic tartrate, from which it is readily distinguished by the action of heat, which chars the tartrate but not the oxalate.

Trihydropotassium oxalate, or *potassium quadroxalate*, $(CO_2)_2H_3K.2Aq$, is more commonly sold as salt of sorrel, and sometimes as salts of lemon. It is even less soluble than the preceding.

Sodium oxalate, $(CO_2Na)_2$, is found in various plants which grow in salt marshes. It is less soluble than potassium oxalate. The alkaline oxalates, when heated, evolve CO and leave carbonates—

$$(CO_2K)_2 = CO + CO(OK)_2.$$

Ammonium oxalate, $(CO_2NH_4)_2.Aq$, occurs in Peruvian guano. It is used in analysis for the precipitation of calcium, and crystallises, in needles, from solution of oxalic acid neutralised with ammonia.

Calcium oxalate, $(CO_2)_2Ca.Aq$, is often found crystallised in plant-cells. Some lichens growing on limestone contain half their weight of calcium oxalate. It is occasionally found in urine and in calculi. Calcium chloride is the best test for oxalic acid, giving a white precipitate insoluble in acetic acid. When heated, $(CO_2)_2Ca = CO + CaCO_3$.

Ferrous oxalate, $(CO_2)_2Fe$, occurs as *oxalite* in brown coal.

Ferric oxalate, $(CO_2)_6Fe_2$, when exposed to sunlight in presence of water, evolves CO_2, and deposits a yellow crystalline precipitate of $(CO_2)_2Fe.2Aq$. Ferric oxalate is used in photography.

Potassium-ferrous oxalate, $(CO_2)_4K_2Fe$, prepared by adding potassium oxalate in excess to ferrous sulphate, is a very powerful reducing agent, useful in photography.

Potassium-chromic oxalate, $(CO_2)_6K_3Cr.3Aq$, is obtained, in crystals so intensely blue as to look black, by dissolving in hot water 1 part of potassium dichromate, 2 parts of hydropotassium oxalate, and 2 parts of oxalic acid. Neither the oxalic acid nor the chromium can be precipitated from this salt by the usual tests.

Potassium-ammonium chromic oxalate, $(CO_2)_{12}K_5NH_4Cr_2.6Aq$, is formed when hydro-ammonium oxalate is substituted for part of the hydropotassium oxalate in preparing the preceding salt, the formula of which should apparently be doubled; it forms blue prisms like the potassium salt.

Potassium-calcium chromic oxalate, $(CO_2)_6KCaCr.3Aq$, is soluble in water, and gives a precipitate of calcium oxalate on adding calcium chloride.

Barium chromic oxalate, $(CO_2)_{12}Ba_3Cr_2.8Aq$, is also a soluble salt, and, when decomposed by sulphuric acid, yields a red solution which probably contains the acid $(CO_2)_{12}H_6Cr_2$ or $H_3(CO_2)_6Cr.Cr(CO_2)_6H_3$.

Potassium-antimony oxalate, $(CO_2)_6K_3Sb.6Aq$, obtained by dissolving precipitated Sb_2O_3 in hydropotassium oxalate, is used in fixing certain colours.

Silver oxalate, $(CO_2Ag)_2$, is obtained as a white precipitate when silver nitrate is added to an oxalate. It explodes slightly when heated, leaving metallic silver.

Oxidising agents easily convert oxalic acid into water and CO_2; if a hot solution of the acid be poured on manganese dioxide, brisk effervescence is caused by the CO_2 produced. A similar result ensues if manganese dioxide be added to the mixture of an oxalate with dilute sulphuric acid.

Nascent hydrogen reduces oxalic acid to glycolic acid—

$$(CO_2H)_2 + H_4 = CH_3O.CO_2H + H_2O.$$

388. Oxalic acid is the representative of the homologous series of acids, $C_nH_{2n}(CO.OH)_2$, known as the oxalic or *succinic series*, which are all dibasic, containing $(CO_2H)_2$. They are all crystalline solids, which cannot be sublimed without partial decomposition, generally yielding CO_2 and an acid of the acetic series. When fused with caustic alkalies they yield carbonates, and a salt of an acid of the acetic series. Many of the acids of this series are formed when fats and oils are oxidised by nitric acid.

389. *Malonic acid*, $CH_2(CO_2H)_2$, is prepared from chloracetic acid, $CH_2Cl.CO_2H$, by converting it into the potassium salt, and boiling this with potassium cyanide, when *potassium cyanacetate*, $CH_2(CN).CO_2K$, is formed. This is boiled with potash, which converts it into potassium malonate; $CH_2(CN).CO_2K + H_2O + KHO = CH_2(CO_2K)_2 + NH_3$. The excess of potash is neutralised by HCl, and calcium chloride added, which precipitates calcium malonate; by boiling this with the molecular proportion of oxalic acid, the calcium is left as oxalate, and the solution deposits tabular crystals of malonic acid. It fuses at 132° C., and afterwards decomposes into CO_2 and acetic acid; $CH_2(CO_2H)_2 = CO_2 + CH_3.CO_2H$. It will be remembered that oxalic acid is decomposed into CO_2, and formic acid, $H.CO_2H$.

Calcium malonate, like the oxalate, is very slightly soluble in water; the silver and lead salts are insoluble.

Malonic acid is found among the products of oxidation of allylene, amylene, and propylene with potassium permanganate.

Succinic acid, $C_2H_4(CO_2H)_2$, is prepared by the fermentation of tartaric acid, which may be regarded as dihydroxysuccinic acid, $C_2H_2(HO)_2(CO_2H)_2$, and becomes reduced to succinic acid.

The tartaric acid is neutralised with ammonia, largely diluted, and mixed with a little potassium phosphate, magnesium sulphate, and calcium chloride, to afford mineral food for the bacteria, which soon grow if the liquid be kept warm (25°–30° C.). The flask should be loosely closed to exclude air. After about two months the ammonium tartrate has become converted into ammonium succinate and carbonate; it is boiled to expel the latter, milk of lime added, and again boiled as long as NH_3 is expelled; the calcium succinate is decomposed by a slight deficiency of dilute sulphuric acid, the liquid filtered from the calcium sulphate, and evaporated to crystallisation.

Succinic acid crystallises in prisms, which require about 20 parts of cold and 3 parts of hot water to dissolve them. It is also soluble in alcohol, but sparingly in ether. When heated, it emits vapour at 120° C., and fuses at 180°; at 235° it is decomposed into water and *succinic anhydride*, $C_2H_4(CO)_2O$, and the vapours provoke coughing in a remarkable way, thus affording a test for the acid. It is very stable, and little affected by oxidising agents. Fusion with KHO converts it into potassium carbonate and propionate—

$$C_2H_4(CO_2H)_2 + 3KHO = CO(OK)_2 + C_2H_5.CO_2K + 2H_2O.$$

Calcium succinate, $C_2H_4(CO_2)_2Ca.3Aq$, is somewhat sparingly soluble in water; it occurs in the bark of the mulberry-tree.

Basic *ferric succinate*, $Fe'''_2(C_4H_4O_4)''_2(OH)'_2$, is precipitated when ferric chloride is added to a succinate; it has a rich brown colour, and its production forms a good test for succinic acid, and is useful in quantitative analysis for separating iron from manganese and some other metals.

Succinic acid was formerly made by distilling refuse amber, which contains it ready formed, in iron retorts. The distillate was decolorised by boiling with nitric acid, and the succinic acid crystallised out. It is also obtained by fermenting, with yeast or old cheese, the impure calcium malate prepared from the berries of the mountain ash (p. 533). After standing for some days at about 35° C., the malate has become converted into a mixture of acetate and succinate—

$$(1)\ C_2H_3.OH(CO_2H)_2 + H_2O = CH_3.CO_2H + 2CO_2 + 2H_2;$$
$$(2)\ C_2H_3.OH(CO_2H)_2 + H_2 = C_2H_4(CO_2H)_2 + H_2O.$$

Malic acid is *hydroxysuccinic acid*, and is reduced by fermentation to succinic acid. Both malic and tartaric acid are reduced to succinic acid by the action of hydriodic acid. Succinic acid has been obtained synthetically by boiling ethene dibromide with potassium cyanide dissolved in alcohol, and boiling the ethene dicyanide thus obtained with KHO dissolved in alcohol—

$$C_2H_4Br_2 + 2KCN = C_2H_4(CN)_2 + 2KBr; \text{ and}$$
$$C_2H_4(CN)_2 + 2KHO + 2H_2O = C_2H_4(CO_2K)_2 + 2NH_3.$$

It will be remembered that malonic acid is obtained from chloracetic acid by similar reactions.

Succinic acid is always produced in small quantity in the fermentation of sugar, and is therefore always present in beer, wine, and vinegar. It is also produced when nitric acid oxidises fatty acids containing four or more carbon atoms. It occurs in unripe grapes, whilst ripe grapes contain tartaric (dihydroxysuccinic) acid. It is found in several plants, such as lettuce, poppies, and wormwood, and in certain lignites. It has also been found in the urine of the horse, goat, and rabbit.

When electrolysed, succinic acid yields ethene, CO_2, and H, as might be expected from its formula, $C_2H_4(CO_2H)_2$.

Iso-succinic acid, which is isomeric with succinic, is obtained from cyanopropionic acid by treatment similar to that which converts cyanacetic acid into malonic acid (p. 530). It resembles malonic acid more than succinic, for it fuses at 130° C., and is decomposed at 150° into CO_2 and propionic acid—

$$C_2H_4(CO_2H)_2 = C_2H_5(CO_2H) + CO_2.$$

Pyrotartaric acid, $C_3H_6(CO_2H)_2$, or *methyl-succinic acid*, $C_2H_3.CH_3(CO_2H)_2$, is obtained by the dry distillation of tartaric acid mixed with powdered pumice-stone to diffuse the heat. The distillate is mixed with water, filtered from oily matter, evaporated on a water-bath, and crystallised from alcohol. Since other products are formed, the change cannot be expressed by a single equation, but if tartaric acid be regarded as dihydroxysuccinic acid, $C_2H_2(HO)_2(CO_2H)_2$, the nature of the transformation is evident. It may also be obtained by heating tartaric acid with strong HCl in a sealed tube to 180° C. It forms prismatic crystals, decomposed by heat into water and pyrotartaric anhydride. Pyrotartaric acid may be synthesised from propene, as succinic acid is from ethene. It is also formed incidentally in many reactions, such as that occurring when gamboge is fused with caustic potash.

390. *Adipic acid*, $C_4H_8(CO_2H)_2$, is prepared by heating iodo-propionic acid with finely divided silver; $2(C_2H_4I.CO_2H) + Ag_2 = 2AgI + C_4H_8(CO_2H)_2$. It crystallises in prisms, and is soluble in water, alcohol, and ether. It is also formed by the action of nitric acid upon some fatty bodies, and by the reduction of saccharic acid, $C_4H_8O_4(CO_2H)_2$, by hydriodic acid.

Pimelic acid, $C_5H_{10}(CO_2H)_2$, is formed as a potassium salt when camphoric acid, $C_8H_{14}(CO_2H)_2$, is fused with potash. It forms crystals soluble in water, alcohol, and ether. When heated, it is decomposed into water and *pimelic anhydride*, $C_5H_{10}(CO)_2O$, an oily liquid boiling at 250° C. Calcium pimelate is precipitated when ammonium pimelate is boiled with calcium chloride, being less soluble in hot water than in cold.

Suberic acid, $C_6H_{12}(CO_2H)_2$, is formed when palm-oil or castor-oil or cork is boiled with nitric acid. It is a crystalline acid, sparingly soluble in cold water, but soluble in hot water and alcohol, subliming to some extent without decomposition.

Azelaic acid, $C_7H_{14}(CO_2H)_2$, also called *anchoic* and *lepargylic acid*, is also obtained by the oxidation of cork, castor-oil, and Chinese wax with nitric acid. It resembles suberic acid, but is more easily soluble in ether. When heated, it evolves suffocating fumes, like succinic acid.

Sebacic acid, or *sebic acid*, $C_8H_{16}(CO_2H)_2$, is prepared as a sodium salt by heating castor-oil with NaHO. The oil is heated for some time with a saturated solution of caustic soda, and the soap thus obtained, after being dried and heated, is dissolved in water and decomposed by HCl, which separates it as a precipitate sparingly soluble in cold water, but crystallising from a hot solution in lustrous scales. Sebacic acid is also formed by the distillation of oleic acid. When distilled with baric hydrate, it yields baric carbonate and octane—

$$C_8H_{16}(CO_2H)_2 + 2Ba(HO)_2 = 2BaCO_3 + C_8H_{18} + 2H_2O.$$

Brassylic acid, $C_9H_{18}(CO_2H)_2$, is formed by the action of the strongest nitric acid on behenolic acid, $C_{21}H_{39}.CO_2H$, which is derived from brassic or erucic acid (p. 518), homologous with oleic acid. It forms very fusible crystals, scarcely soluble in water, but dissolving easily in ether.

Roccellic acid, $C_{15}H_{30}(CO_2H)_2$, is extracted from the litmus lichen, *Roccella tinctoria*, and others of the same kind, by digesting with dilute ammonia, precipitating by calcium chloride, and decomposing the calcium roccellate by HCl. The acid is insoluble in water, but dissolves in alcohol and ether, crystallising in plates which fuse easily and volatilise in part undecomposed.

391. *Fumaric acid*, $C_2H_2(CO_2H)_2$, is obtained by heating malic acid to 150° C. as long as water distils over; $C_2H_3.OH(CO_2H)_2 = C_2H_2(CO_2H)_2 + H_2O$. The residue is treated with cold water to extract unaltered malic acid, and the fumaric acid is crystallised from hot water or alcohol. When heated to 200° C. it partly sublimes undecomposed, and the rest decomposes into water and malæic anhydride. Heated with much water to 150°, it is reconverted into malic acid. NaHO at 100° slowly converts it into sodium malate. Nascent hydrogen, from water and sodium-amalgam, converts it into succinic acid, $C_2H_4(CO_2H)_2$. Hydriodic acid effects the same change, iodine being liberated. The fumarates of barium, calcium, and lead are sparingly soluble. Silver fumarate is very insoluble, and explodes when heated. The alkaline fumarates, when electrolysed, yield acetylene, C_2H_2, carbon dioxide, which forms a carbonate, and hydrogen, thus justifying the formula given for the acid. Fumaric acid is found in several plants, especially in fumitory, Iceland moss, truffles, and other fungi. Malic acid may be converted into fumaric acid by boiling it with strong HCl, or by heating it with a little water to 180° C. in a sealed tube. Fumaric acid is not oxidised by boiling with nitric acid.

Malæic acid, isomeric with fumaric acid, is produced when malic acid is quickly distilled. It is crystalline, and easily decomposed by heat into water and malæic anhydride. It differs from fumaric acid by the solubility of its barium and calcium salts. It is converted into fumaric acid if kept in fusion for some time, or if boiled with dilute acids.

Pyrocitric acids, $C_3H_4(CO_2H)_2$, include *citraconic*, *itaconic*, and *mesaconic* acids. When citric acid is distilled, the distillate separates into two layers, and deposits crystals of itaconic acid; the lower layer is an aqueous solution of citraconic acid, from which this acid may be crystallised, whilst the upper layer consists of citraconic anhydride. If citraconic acid be heated for some time with dilute HNO_3 or strong HCl, it is converted into mesaconic acid. These acids are isomeric, but they differ in solubility, mesaconic requiring about 40 parts of cold water, itaconic about 20 parts, and citraconic only 1 part. The crystals of mesaconic acid fuse at 208° C., itaconic at 161°, and citraconic at 80°. They are all three reduced by nascent hydrogen to pyrotartaric acid, $C_3H_6(CO_2H)_2$, a member of the succinic series of acids. They combine with the haloid acids to form isomeric substitution products of pyrotartaric acid; thus—

$$C_3H_4(CO_2H)_2 + HBr = C_3H_5Br(CO_2H)_2.$$

Hydromuconic acid, $C_4H_6(CO_2H)_2$, is prepared from chloromuconic acid by the action of water and sodium-amalgam. Chloromuconic acid is formed by acting with water on the chloromuconic dichloride resulting from the treatment of mucic acid with phosphoric chloride—

$$C_4H_8O_4(CO_2H)_2 + 6PCl_5 = C_4H_2Cl_2(COCl)_2 + 6POCl_3 + 8HCl;$$
$$C_4H_2Cl_2(COCl)_2 + 2H_2O = C_4H_2Cl_2(CO_2H)_2 + 2HCl;$$
$$C_4H_2Cl_2(CO_2H)_2 + 2H_2O + 3Na_2 = C_4H_6(CO_2Na)_2 + 2NaCl + 2NaHO.$$

The acid is easily obtained from the sodium salt. It crystallises in sparingly soluble prisms. By the action of nascent hydrogen it is converted into adipic acid, $C_4H_8(CO_2H)_2$, the isologous acid in the succinic series.

392. *Tartronic* or *hydroxymalonic acid*, $CH.OH(CO_2H)_2$, is formed by the action of nascent hydrogen on mesoxalic acid, $C(HO)OH(CO_2H)_2$, which is hydroxytartronic acid, and is a product of the oxidation of uric acid. It forms crystals which are decomposed by heat into water, CO_2, and an amorphous substance known as glycolide, which is also produced by the action of heat on glycolic acid; $CH.OH(CO_2H)_2 = CO_2 + H_2O + C_2H_2O_2$ (*glycolide*). Tartronic acid was first obtained by heating solution of dinitrotartaric acid—

$$C_2H_2(ONO_2)_2(CO_2H)_2 = CH.OH(CO_2H)_2 + N_2O_3 + CO_2.$$

It is also formed when glucose is oxidised by an alkaline cupric solution. Barium tartronate, from which the acid is readily obtained, may be prepared by heating glyoxalic acid with potassium cyanide and baryta-water—

$$CH(OH)_2CO_2H + KCN + Ba(HO)_2 = CH.OH.(CO_2)_2Ba + KOH + NH_3.$$

Mesoxalic or *hydroxytartronic acid*, $C(HO).OH(CO_2H)_2$, is made from alloxan, a product of the oxidation of uric acid by nitric acid. Solution of alloxan is heated with baryta-water added carefully, till barium alloxanate is precipitated; alloxan, $(CO)_2(CONH)_2 + H_2O =$ alloxanic acid, $CO.CONH.CONH_2.CO_2H$. When barium alloxanate is boiled with much water, it is converted into the mesoxalate, which crystallises on cooling, leaving urea in solution—

$$CO.CONH.CONH_2.CO_2H + 2H_2O = C(HO).OH(CO_2H)_2 + CO(NH_2)_2.$$

The barium mesoxalate, decomposed by sulphuric acid, yields crystals of mesoxalic acid, which are very soluble in water. It reduces silver oxide on boiling, and is converted into oxalic acid—

$$C(HO).OH(CO_2H)_2 + Ag_2O = (CO_2H)_2 + Ag_2 + CO_2 + H_2O.$$

Malic or *hydroxysuccinic acid*, $C_2H_3.OH(CO_2H)_2$, is extracted from the juice of the unripe berries of the mountain ash. The juice is boiled, filtered, nearly neutralised with milk of lime, and boiled, when calcium malate, $C_2H_3.OH(CO_2)_2Ca.Aq$, is precipitated in minute crystals. This is dissolved, to saturation, in hot nitric acid diluted with ten times its weight of water. On cooling, crystals of hydrocalcium malate, $[C_2H_3.OH(CO_2H).CO_2]_2.Ca.8Aq$, are deposited. These are dissolved in hot water, and decomposed by lead acetate, when lead malate is precipitated; this is suspended in water, and H_2S passed, when PbS remains precipitated, and malic acid is found in solution, from which it crystallises, though not very readily, in tufts of deliquescent needles. It fuses at 100° C., and at a higher temperature yields a feathery sublimate of maleic and fumaric acids (p. 532) and of their anhydrides. When long boiled with HCl, it is converted into fumaric acid and water. Hydriodic acid reduces it to succinic acid—

$$C_2H_3.OH(CO_2H)_2 + 2HI = C_2H_4(CO_2H)_2 + H_2O + I_2.$$

Oxidation by chromic acid converts malic acid into malonic, $CH_2(CO_2H)_2$. Fused with potash, it yields acetate and oxalate—

$$C_2H_3.OH(CO_2K)_2 + KOH = CH_3.CO_2K + (CO_2K)_2 + H_2.$$

Malic acid is one of the chief natural vegetable acids, occurring in apples, gooseberries, currants, &c. Cherries and rhubarb contain hydropotassium malate; $C_2H_3.OH(CO_2H)(CO_2K)$. Tobacco contains the hydrocalcium malate. Normal calcium malate, $C_2H_3.OH(CO_2)_2Ca$, is less soluble in hot water, and is therefore precipitated, like calcium citrate, on neutralising the acid with lime-water and boiling. Lead malate forms a white precipitate containing 3Aq, which is distinguished by fusing under water to a gummy mass, becoming crystalline on cooling.

Natural malic acid, in strong solution, rotates the plane of polarisation to the right, and a weak solution rotates it to the left; but the malic acid prepared from succinic acid is inactive in this respect. This *inactive malic acid* is obtained by boiling bromosuccinic acid with water and silver oxide—

$$C_2H_3Br(CO_2H)_2 + AgOH = C_2H_3.OH(CO_2H)_2 + AgBr.$$

Bromosuccinic acid is obtained by heating succinic acid with water and a molecular weight of bromine to 150° C., in a sealed tube.

393. *Tartaric* or *dihydroxysuccinic acid*, $C_2H_2(OH)_2(CO_2H)_2$, is prepared from the *argol*, or *tartar*, deposited in crystalline crusts during the fermentation of grape-juice. This (45 ounces) is boiled with (2

gallons) water, and neutralised by adding (12½ ounces) powdered chalk, which converts the hydropotassium tartrate of the argol into calcium tartrate and potassium tartrate—

$$2C_4H_4O_6KH + CaCO_3 = C_4H_4O_6K_2 + C_4H_4O_6Ca + H_2O + CO_2.$$

The potassium tartrate dissolves and the calcium tartrate precipitates. Solution of calcium chloride (13½ oz. dissolved in 2 pints of water) is then added, to precipitate the potassium tartrate as calcium tartrate; $C_4H_4O_6K_2 + CaCl_2 = C_4H_4O_6Ca + 2KCl$. The calcium tartrate is strained off, washed, and heated for half an hour with dilute sulphuric acid (13 fluid ounces of acid in 3 pints of water), when calcium sulphate remains undissolved, and tartaric acid may be crystallised by evaporating the filtered solution; $C_4H_4O_6Ca + H_2SO_4 = C_4H_4O_6H_2 + CaSO_4$. The crude acid is dissolved in water, decolorised by animal charcoal, and again crystallised. A little sulphuric acid is generally added to promote the formation of large crystals. These often contain lead derived from the evaporating pans.

Properties of tartaric acid.—The crystals are monoclinic prisms, very soluble in water, and fairly so in alcohol, but nearly insoluble in ether. When heated to 135° C. it fuses, and becomes an amorphous deliquescent mass of *metatartaric acid*, isomeric with it. At 145° it becomes *tartralic acid*, $C_8H_{10}O_{11}$, two molecules of the acid having lost a molecule of water; at 180° it yields *tartrelic acid*, $C_8H_8O_{10}$, and *tartaric anhydride*, which is isomeric with it. All these may be reconverted into tartaric acid by digestion with water. On further heating, it undergoes destructive distillation, yielding acetic, *pyroracemic*, $C_3H_4O_3$, *pyrotartaric*, $C_5H_8O_4$, *pyrotritartaric*, $C_7H_8O_3$, and formic acids, together with *dipyrotetracetone*, $C_8H_{12}O_2$, which has a peculiar odour, like burnt sugar, by which tartaric acid may be recognised. Acetone, aldehyd, carbonic oxide and dioxide are also among the products.

Fused KHO converts tartaric acid into acetate and oxalate. Boiled with nitric acid, much of it is oxidised to oxalic acid. Distilled with sulphuric acid and MnO_2, or $K_2Cr_2O_7$, it yields formic acid and CO_2.

Hydriodic acid, in strong aqueous solution, heated to 120° C. with tartaric acid, in a sealed tube, reduces it to malic acid, which is again reduced to succinic acid—

$$C_2H_2(OH)_2(CO_2H)_2 + 2HI = C_2H_3.OH.(CO_2H)_2\ (\textit{malic acid}) + H_2O + I_2.$$
$$\text{And } C_2H_3.OH.(CO_2H)_2 + 2HI = C_2H_4(CO_2H)_2\ (\textit{succinic acid}) + H_2O + I_2.$$

Tartaric acid is one of the most important vegetable acids, being often found in fruits associated with malic acid. It is dibasic, and is remarkable for forming a very sparingly soluble potassium salt, which is precipitated in minute crystals when almost any salt of potassium is added to tartaric acid, and stirred with a glass rod, when the precipitate attaches itself to the lines of friction.

394. *Hydropotassium tartrate*, $HKC_4H_4O_6$, or *cream of tartar*, is prepared by recrystallising argol from hot water, which dissolves $\frac{1}{15}$th of its weight, and only retains $\frac{1}{200}$th on cooling. It is nearly insoluble in alcohol, which precipitates it from the aqueous solution, and this explains its separation from the grape-juice, as the proportion of alcohol increases during the fermentation. It dissolves easily in acids, and in alkalies, which convert it into normal tartrate, $K_2C_4H_4O_6$. When heated, it evolves the burnt-sugar odour, and leaves a black mass of charcoal and potassium carbonate (*salt of tartar*).

Sodio-potassium tartrate, $NaKC_4H_4O_6.4Aq$, *Rochelle* or *Seignette's salt*, is prepared by neutralising a boiling solution of sodium carbonate with cream of tartar, when it crystallises on cooling, in fine rhombic prisms. It is useful in medicine.

Calcium tartrate, $CaC_4H_4O_6.4Aq$, occurs in grapes and in senna leaves. It is sparingly soluble in water, and is precipitated when $CaCl_2$ is added to an ammoniacal solution of a tartrate. It is soluble in potash and in ammonium chloride.

Cupric tartrate, $CuC_4H_4O_6.3Aq$, is sparingly soluble in water, but dissolves in alkalies to a deep blue solution, in which two atoms of the alkali metal have displaced H_2. Such a solution is often used in analysis, as *alkaline cupric solution*, or *Fehling's test*. Tartaric acid behaves in a similar way with several other metals, retaining them in alkaline solutions when they would otherwise be precipitated as hydrates; in the cases of aluminium and iron, this is turned to account in analysis.

Silver tartrate, $Ag_2C_4H_4O_6$, is precipitated by silver nitrate from a normal tartrate; it dissolves in ammonia, and the solution deposits metallic silver when heated, the tartaric acid being oxidised to carbonic and oxalic acids. This is taken advantage of in some processes for silvering mirrors.

Potassium-antimonyl-tartrate, $K.SbO.C_4H_4O_6$, or *tartar-emetic*, is prepared by boiling cream of tartar (6 oz.) with water (2 pints) and (5 oz.) antimonious oxide—

$$Sb_2O_3 + 2KHC_4H_4O_6 = 2KSbOC_4H_4O_6 + H_2O.$$

From the filtered solution, on cooling, the salt crystallises in rhombic prisms, of the formula $2KSbOC_4H_4O_6.Aq$. It is soluble in three parts of hot water, and in fifteen parts of cold water. The crystals lose their water of crystallisation at 100° C., and when heated over 200° the emetic loses the elements of another molecule of water, and becomes $KSbC_4H_2O_6$, which is reconverted into emetic by boiling with water. When barium chloride is added to tartar-emetic, a precipitate is formed, according to the equation—

$$2KSbOC_4H_4O_6 + BaCl_2 = Ba(SbOC_4H_4O_6)_2 + 2KCl.$$

By decomposing this barium salt with sulphuric acid, an acid solution is obtained, which soon deposits antimonious hydrate, but if it be neutralised with potash before decomposition takes place, it yields tartar-emetic. Hence it would seem that the emetic is the potassium salt of the acid $H(SbOC_4H_4O_6)$ or $C_2H_2(OH)_2(CO_2)_2SbO.H$, which is derived from tartaric acid by replacing one atom of H in the $(CO_2H)_2$ by the monad radical *antimonyl*, $Sb'''O''$. The emetic acid has been named *tartryl antimonious acid*, so that tartar-emetic would be *potassium tartryl antimonite*. Other tartryl-antimonites have been obtained. By dissolving Sb_2O_3 in tartaric acid, and adding alcohol, a crystalline precipitate of antimonyl tartrate, $(SbO)_2C_4H_4O_6$, is obtained, and this becomes tartar-emetic when boiled with normal potassium tartrate—

$$(SbO)_2C_4H_4O_6 + K_2C_4H_4O_6 = 2KSbOC_4H_4O_6.$$

The antimony in tartar-emetic may be replaced by arsenic and by boron.

When excess of Sb_2O_3 is boiled with solution of tartaric acid, and the liquid evaporated to a syrup, it deposits crystals of $H.SbO.C_4H_4O_6$, which is decomposed by water, and appears to be identical with the tartryl-antimonious acid.

Tartaric acid may be obtained artificially by boiling silver dibromo-succinate with water—

$$C_2H_2Br_2(CO_2Ag)_2 + 2H_2O = C_2H_2(OH)_2(CO_2H)_2 + 2AgBr.$$

395. *Racemic acid*, isomeric with tartaric, is prepared by heating tartaric acid with about one-tenth of its weight of water in a sealed tube to 175° C. for about thirty hours. It differs from tartaric acid in the form of its crystal (a triclinic prism), in containing a molecule of water of crystallisation, in being much less soluble in water, and in being less easily fusible (202° C.). Moreover, its solution in water has no action on polarised light, whilst tartaric acid is dextrorotatory.

Hydropotassium racemate is more soluble than the tartrate.

Calcium racemate, $CaC_4H_4O_6.4Aq$, differs from the tartrate in being insoluble in acetic acid, and nearly so in ammonium chloride. Precipitated calcium tartrate becomes crystalline on standing, and is then insoluble in acetic acid, having probably become converted into the racemate. When solution of calcium tartrate in ammonium chloride is briskly stirred, a precipitate insoluble in acetic acid is deposited on the lines of friction; this is probably calcium racemate.

Solution of racemic acid is precipitated by calcium sulphate, which does not precipitate tartaric acid unless previously neutralised.

Racemic acid is found mixed with the tartaric acid extracted from certain samples of argol, and its crystals may be distinguished from those of tartaric acid by the cloudy appearance which they assume at 100° C., due to the loss of their water of crystallisation.

The *sodium-ammonium racemate*, $NaNH_4C_4H_4O_6$, has the same crystalline form as the tartrate, but whilst all the crystals of this salt are exactly alike, those of the racemate are right-handed and left-handed. When these are picked out, and the acid extracted from them, the right-handed crystals yield ordinary dextrorotatory tartaric acid, whilst the left-handed crystals yield an acid of the same composition, which is just as strongly lævorotatory; hence this is called *lævotartaric* acid. If equal weights of the dextro- and lævo-tartaric acid, in solution, be mixed, heat is evolved, the solution loses its action on polarised light, and yields crystals of racemic acid.

Mesotartaric acid, or inactive tartaric acid, is isomeric with tartaric acid, but is without action on polarised light, and has different properties from those of racemic acid. It is obtained by heating 30 parts of tartaric acid and 4 parts of water to 165° C. for two hours, in a sealed tube. The mass is dissolved in water, when racemic acid crystallises first. The unaltered tartaric acid is precipitated as hydropotassium tartrate, leaving the more soluble mesotartrate in solution. Mesotartaric acid crystallises in rectangular tables with one molecule of water. It is rather less soluble than tartaric. The normal and acid potassium salts do not crystallise. Calcium mesotartrate, $CaC_4H_4O_6.3Aq$, is at first a flocculent precipitate, which soon becomes crystalline; it is insoluble in acetic acid. Free mesotartaric acid is not precipitated by calcium sulphate. Other inactive tartaric acids are known.

The acid obtained by the action of water on the silver dibromo-succinate, though having the same composition as tartaric acid, is really a mixture of racemic and mesotartaric acids. When dextrorotatory tartaric acid is reduced by hydriodic acid (p. 534), it yields a dextrorotatory malic acid; but when racemic acid is employed, an inactive malic acid is produced, which can be decomposed, like racemic acid, into a dextrorotatory and a lævorotatory acid.

396. *Phthalic acid*, $C_6H_4(CO_2H)_2$, is prepared by oxidising naphthalene tetrachloride with nitric acid. Naphthalene, $C_{10}H_8$, is carefully mixed, on paper, with 2 parts, by weight, of potassium chlorate, and added, *in small portions*, to 10 parts of strong hydrochloric acid. The naphthalene tetrachloride, $C_{10}H_8Cl_4$, thus formed, is washed with water till free from acid, and allowed to dry. It is introduced into a flask and treated with strong nitric acid (sp. gr. 1.45), which must be very gradually added, amounting to ten times the weight of naphthalene taken. The mixture is heated till all is dissolved, the nitric acid boiled off, and the residue distilled, when *phthalic anhydride* distils over and is converted into phthalic acid by dissolving in hot water and crystallising; $C_6H_4(CO)_2O + H_2O = C_6H_4(CO_2H)_2$.

Phthalic acid crystallises in rhombic prisms which are easily fusible, and readily decomposed into water and the anhydride. It is sparingly soluble in cold water, but dissolves readily in hot water, in alcohol, and in ether. When calcium phthalate is heated with lime to 340° C., it yields benzoate and carbonate of calcium (p. 519). Chromic acid oxidises phthalic acid completely into CO_2 and H_2O. Phthalic acid is found among the products of oxidation of anthracene, alizarin, and purpurin with nitric acid or MnO_2 and H_2SO_4.

Isouritic acid, $C_7H_6(CO_2H)_2$, is obtained by fusing gamboge with potash. It crystallises in prisms soluble in hot water.

Cumidic acid, $C_6H_2(CH_3)_2(CO_2H)_2$, is prepared by boiling durene, $C_6H_2(CH_3)_4$, with dilute nitric acid. It is sparingly soluble in water, but dissolves in alcohol. *Cumylic acid*, $C_6H_2(CH_3)_3.CO_2H$, which is formed at the same time, fuses at 150° C. and sublimes in needles, while cumidic acid does not fuse, and sublimes in scales.

Tricarballylic acid, $C_3H_5(CO_2H)_3$, may be obtained by heating citric acid with hydriodic acid; $C_3H_4(HO)(CO_2H)_3 + 2HI = C_3H_5(CO_2H)_3 + H_2O + I_2$. This acid may also be built up from glycerin, $C_3H_5(OH)_3$, by distilling it with PI_4 to obtain C_3H_5I, converting this into glyceryl tribromide, $C_3H_5Br_3$, by bromine, and heating the tribromide with alcohol and potassium cyanide to obtain *tricyanhydrin*, or *glyceryl tricyanide*, $C_3H_5(CN)_3$, which yields potassium tricarballylate and ammonia when boiled with potash; $C_3H_5(CN)_3 + 3KHO + 3H_2O = C_3H_5(CO_2K)_3 + 3NH_3$.

The calcium salts of tricarballylic, citric, and aconitic acids occur in the deposit formed in the stills of beet-sugar manufactories. Tricarballylic acid crystallises in rhombic prisms, which are easily soluble in water and alcohol.

397. *Citric acid*, $C_3H_4(HO)(CO_2H)_3$, or *hydroxytricarballylic acid*, is prepared from lemon-juice, by heating it and adding chalk as long as effervescence takes place; this precipitates part of the acid as calcium citrate, leaving the rest in solution as an acid salt; this is precipitated by adding milk of lime, and boiling. The calcium citrate is washed with boiling water, decomposed by exactly the required quantity of dilute sulphuric acid, the liquid filtered from the calcium sulphate, and evaporated to crystallisation. It is sometimes recommended to ferment the lemon-juice with yeast for two days, and to filter before adding the chalk.

Properties of citric acid.—The crystals contain one molecule of water, and are rhombic prisms, very soluble in water, and fairly so in alcohol and ether. It fuses at 100° C., and loses its water of crystallisation at 130°. Heated to 175°, it loses H_2O and becomes aconitic acid, $C_3H_3(CO_2H)_3$. When further heated, this loses CO_2, and *itaconic acid* distils over, crystallising in the neck of the retort; $C_3H_3(CO_2H)_3 = CO_2 + C_3H_4(CO_2H)_2$. The liquid portion of the distillate contains *citraconic acid* isomeric with itaconic, into which it is converted by heating its concentrated solution to 120° C. Oxidising agents convert citric acid into acetone and its derivatives. When dehydrated by phosphoric or sulphuric acid, it also yields acetone, together with CO and CO_2; $C_3H_4(HO)(CO_2H)_3 = 2CO_2 + CO + H_2O + CH_3.CO.CH_3$ (*acetone*). Fusion with potash converts it into acetate and oxalate—

$$C_3H_4(HO)(CO_2H)_3 + 4KHO = 2(CH_3.CO_2K) + (CO_2K)_2 + 3H_2O.$$

Solution of citric acid, mixed with excess of lime-water, gives no precipitate in the cold, distinguishing it from tartaric and oxalic acid; but when heated, it deposits *calcium citrate*, $Ca_3(C_6H_5O_7)_2.4Aq$, which is more soluble in cold than in hot water, but is insoluble in potash, which dissolves calcium tartrate; ammonium chloride and acetic acid dissolve it.

Magnesium citrate, $Mg_3(C_6H_5O_7)_2.14Aq$, is easily soluble in water; mixed with $NaHCO_3$, citric acid, and sugar, and rendered granular by moistening with alcohol and drying, it forms *effervescent citrate of magnesia.*

Ferric citrate, $Fe_2(C_6H_5O_7)_2.6Aq$, used in medicine, forms transparent red scales prepared by dissolving ferric hydrate in citric acid, and evaporating. *Ferric ammonio-citrate*, $Fe_2(NH_4)_3(C_6H_5O_7)_3$, is also used medicinally.

Citric acid is found in many fruits, associated with malic and tartaric acid. The citrates of potassium and calcium are present in many vegetables, and in the indigo and tobacco plants.

Citric acid may be built up from acetone by the following steps:—

(1) $CH_3.CO.CH_3 + Cl_4 = 2HCl + CH_2Cl.CO.CH_2Cl$ (*dichloracetone*); (2) by heating this with strong hydrocyanic acid, it is converted into *dichloracetone cyanhydrate*, $CH_2Cl.C.OH.CN.CH_2Cl$; (3) this last, acted on by HCl and 2HOH, yields NH_4Cl and *dichloracetonic acid*, $CH_2Cl.C.OH.CO_2H.CH_2Cl$; (4) on treating this with potassium cyanide, it gives 2KCl and *dicyanacetonic acid*, $CH_2CN.C.OH.CO_2H.CH_2CN$; and (5) by the action of 2HCl and 4HOH, this is converted into $2NH_4Cl$ and citric acid, $CH_2.CO_2H.C.OH.CO_2H.CH_2.CO_2H$.

Aconitic acid, $C_3H_3(CO_2H)_3$, is obtained by heating citric acid in a retort till oily drops appear in the neck, and extracting the mass with ether, which leaves the unaltered citric acid undissolved. On evaporating the ether, aconitic acid is left in small crystals, easily soluble in water and alcohol. It is distinguished from citric acid by not precipitating when boiled with excess of lime-water.

Aconitic acid is found in monkshood (*Aconitum napellus*), beet-root, and sugar-cane, and in some other plants.

Meconic acid, $C_4HO(CO_2H)_3$, is extracted from opium by digesting it with hot water, neutralising the solution with calcium carbonate, and adding calcium chloride, which precipitates *hydrocalcium meconate*, $HCaC_7HO_7.Aq$, from which meconic acid may be crystallised by dissolving it in hot dilute HCl. It crystallises in plates containing three molecules of water of crystallisation, dissolving rather sparingly in cold water, but easily in hot water and in alcohol. Ether dissolves it sparingly. When heated, it loses CO_2, and becomes *comenic acid*, $C_6H_4O_5$, and when further heated, *pyrocomenic*, $C_5H_4O_3$. Long boiling with water also converts meconic into comenic acid. Solution of meconic acid gives a fine red colour with ferric chloride, not bleached by mercuric chloride. With silver nitrate, it gives a white precipitate of *hydrodiargentic meconate*, $HAg_2C_7HO_7$, but if a drop of ammonia be added, and the liquid boiled, the precipitate becomes bright yellow *normal silver meconate*, $Ag_3C_7HO_7$.

Meconic acid is closely related, by its composition, to *chelidonic acid*, $C_4H(CO_2H)_3$, an acid obtained from celandine (*Chelidonium majus*), which belongs to the same botanical order as the opium poppy, which yields meconic acid; this may be represented as *hydroxychelidonic acid*, $C_4HO(CO_2H)_3$.

398. ACIDS CONTAINING NITROGEN.—*Hydrocyanic* or *prussic acid*, HCN, is prepared, in aqueous solution, by distilling potassium ferrocyanide (*prussiate of potash*) with dilute sulphuric acid. 50 grammes of the crystallised ferrocyanide are dissolved in 200 cubic centimetres of warm water in a flask or retort connected with a good condenser. 20 c.c. of strong sulphuric acid are diluted with 60 c.c. of water, cooled, and added to the solution of ferrocyanide; heat is applied by a ring-burner to avoid bumping, until about 140 c.c. of liquid have passed into the receiver.

The potassium ferrocyanide is $K_4Fe''(CN)_6.3Aq$, and, when heated with dilute sulphuric acid, it gives up half of the cyanogen, CN, as hydrocyanic acid, leaving the remainder combined with the iron and half of the potassium as *potassio-ferrous ferrocyanide*, $K_2Fe''.Fe''(CN)_6$, a yellow salt which quickly becomes blue when exposed to air, oxygen being absorbed and *Prussian blue*, or *ferric ferrocyanide*, $Fe'''_4.3Fe''(CN)_6$, being produced. The following equation represents the preparation of hydrocyanic acid: $2K_4FeCy_6 + 6H_2SO_4 = 6HCy + K_2Fe''_2Cy_6 + 6KHSO_4$.

Hydrocyanic acid is generally used in the diluted state, but it may be obtained anhydrous by gently heating the diluted acid in a retort connected with a condenser cooled by iced water, and receiving the distillate in a bottle cooled in ice and containing fused calcium chloride in coarse powder. This bottle is afterwards placed in a water-bath connected with a receiver cooled in ice and salt, and gently heated, when the pure hydrocyanic acid distils over. The anhydrous HCy may also be obtained by passing dry H_2S gas into a long tube filled with mercuric cyanide and connected with a receiver cooled in ice and salt; the operation must be stopped when an inch or two of mercuric cyanide remains undecomposed, to avoid contamination of the HCy with H_2S; $HgCy_2 + H_2S = HgS + 2HCy$.

Properties of hydrocyanic acid.—A colourless liquid, sp. gr. 0.7, which evaporates rapidly, so that a few drops in a watch-glass are solidified by the cold of evaporation, the freezing point being $-15°$ C. The acid boils at $27°$ C., giving a vapour which burns with a purple flame. The smell of the vapour is quite characteristic, and is compared by some to a faint odour of almonds; it generally produces a sensation of dryness at the back of the throat. The inhalation of the vapour, unless largely diluted with air, is very dangerous, and an extremely small quantity of the acid taken internally generally kills immediately. When the pure acid is mixed with an equal volume of water, a contraction ensues, amounting to about one-twentieth of the total volume, and *cold* is produced. The aqueous acid is decomposed when exposed to light, depositing a brown substance, whilst ammonium formate and other products are found in solution; $HCN + 2H_2O = NH_4.CO_2H$. A trace of sulphuric acid, which generally splashes over in preparing prussic acid, prevents this decomposition. Acids and alkalies, when boiled with the acid, convert the HCN into formic acid and ammonia.

The acid properties of HCy are very feeble; it hardly reddens litmus, and does not destroy the alkaline reaction of the alkalies or their carbonates. The salts formed by displacing its hydrogen by alkali-metals are easily decomposed by water and carbonic acid, and therefore smell of HCy, but the cyanides formed by many of the metals are very stable bodies.

Although HCy is so much more easily liquefied than HCl, its vapour continually escapes even from a weak aqueous solution, so that the strength is diminished every time the stopper is removed from the bottle; it thus happens that the weak prussic acid (2 per cent.) dispensed by the druggist, is sometimes found to have become nearly pure water.

Hydrocyanic acid is found in laurel-water, and in water distilled from the kernels of many stone-fruits, such as peach, apricot, and plum. In these cases it appears to be produced from amygdalin (see p. 504).

Hydrocyanic acid is produced synthetically by passing a succession of electric sparks through a mixture of nitrogen with an equal volume of acetylene, this being itself produced by carbon intensely heated in hydrogen (p. 93). HCy is also found among the products of distillation of coal, and occurs in imperfectly purified coal-gas.

Tests for hydrocyanic acid.—Silver nitrate produces a white precipitate of silver cyanide, AgCN, which is dissolved by boiling with strong nitric acid, and precipitated in microscopic needles, $AgCN.2AgNO_3$, on cooling. *Prussian-blue test:* Add potash in slight excess, to form KCy; then add ferrous sulphate solution (which always contains ferric sulphate), to form potassium ferrocyanide; $6KCy + Fe''SO_4 = K_4Fe''Cy_6 + K_2SO_4$;

this acts on the ferric sulphate, and produces ferric ferrocyanide, or Prussian blue; $3K_4Fe''Cy_6 + 2Fe'''_2(SO_4)_3 = Fe'''_4(Fe''Cy_6)_3 + 6K_2SO_4$. Finally, add hydrochloric acid in excess, to neutralise the excess of potash, which decomposes the blue. *Sulphocyanide test:* Add yellow ammonium sulphide (which contains some disulphide), to form ammonium sulphocyanide; $HCN + (NH_4)_2S_2 = NH_4CNS + NH_4HS$; evaporate till the smell of ammonium hydrosulphide has disappeared, and add ferric chloride, which will produce the blood-red colour of ferric sulphocyanide, bleached on adding mercuric chloride. A very fugitive purple colour is due to ammonium thiosulphate produced by the action of air, and does not indicate HCy.

The cyanides and other important derivatives of hydrocyanic acid will be considered under the head of *Cyanogen compounds.*

399. *Picric* or *carbazotic acid*, or *trinitrophenol*, $C_6H_2(NO_2)_3OH$, is prepared by the action of nitric acid on phenol. Ten grms. of phenol (crystallised carbolic acid fused by gently heating) are gradually added to 50 c.c. of ordinary nitric acid, and gently heated. When the violent action is over, 20 c.c. of strongest nitric acid are added, and the mixture boiled as long as much red gas is disengaged. On cooling, a crystalline mass of picric acid is obtained, which is purified by dissolving in boiling water, filtering, and crystallising. It is deposited in yellow plates or prisms, which are sparingly soluble in cold water, but more easily on heating, imparting a bright yellow colour to a large volume of water; alcohol dissolves it readily. Its solution has an intensely bitter taste (whence its name), and stains the skin and other organic matters yellow, which is turned to account in dyeing silk and wool. When heated, the crystals fuse at 122° C., with partial sublimation, and explode slightly at a higher temperature, in consequence of the sudden formation of gas and evolution of heat by the action of the NO_2 upon the C and H. The conversion of phenol into picric acid by the action of nitric acid may be represented by the equation—

$$C_6H_5.OH + 3(HO.NO_2) = C_6H_2(NO_2)_3OH + 3HOH.$$

Picric acid is one of the very few acids which form sparingly soluble potassium salts; a cold saturated aqueous solution of picric acid is even a better test for potassium than tartaric acid, giving, especially on stirring, a yellow adherent crystalline precipitate of *potassium picrate*, $C_6H_2(NO_2)_3OK$. This salt explodes violently when heated or struck, and has been used as an explosive. *Ammonium picrate* is also a very explosive salt. Picric acid precipitates several of the alkaloids. An alcoholic solution of picric acid forms crystalline compounds with several hydrocarbons in alcoholic solution, particularly with benzene, naphthalene, and anthracene. Reducing agents, such as glucose, in alkaline solutions, convert picric acid into *picramic acid*, $C_6H_2(NO_2)_2.NH_2.OH$, which forms red salts. Gently heated with solution of chloride of lime, picric acid yields *chloropicrin*, or *nitrochloroform*, $C.NO_2.Cl_3$, recognised by its pungent tear-provoking odour.

Picric acid is a very common product of the action of nitric acid upon organic substances; indigo, silk, and many resins furnish it in considerable quantity, especially the fragrant red resin known as *Botany Bay gum*, obtained from one of the grass-trees of New South Wales, which is sometimes used for preparing picric acid. It is said that picric acid is used as a *hop-substitute* in beer; its presence would be shown by the fast yellow colour imparted to a thread of white wool soaked in the warm liquid.

400. *Hippuric acid*, or *benzoyl-glycocine*, or *benzamidacetic acid*, $C_8H_8NO.CO_2H$, is prepared from the urine of horses or cows (preferably the latter) by evaporating it to about an eighth of its bulk and adding an excess of hydrochloric acid. On standing, long prisms of hippuric acid are deposited, which may be decolorised by dissolving in boiling water and adding a little chlorine-water, when the colourless acid will crystallise out on cooling. If the animal has undergone much exercise, or the urine has decomposed, benzoic acid is obtained instead of hippuric, and if a dose of benzoic acid be taken, it will be found as hippuric acid in human urine, which contains naturally but a minute proportion.

The relationship between the two acids is shown by the following reactions:—Benzoic acid, $C_6H_5.CO.OH$, distilled with PCl_3, yields benzoyl chloride, $C_6H_5.CO.Cl$ (see p. 520); acetic acid, $CH_3.CO_2H$, acted on by chlorine, yields *chloracetic acid*, $CH_2Cl.CO_2H$; this last, under the action of ammonia, gives *amidacetic acid*, $CH_2NH_2.CO_2H$, and HCl; the silver amidacetate, $CH_2NH_2.CO_2Ag$, decomposed by benzoyl chloride, yields AgCl and $CH_2.NH_2.CO_2.C_7H_5O$, which last is benzamidacetic acid, or hippuric acid. When boiled with acids or alkalies, hippuric acid undergoes hydrolysis, and yields amidacetic acid (*glycocine*) and benzoic acid; $CH_2.NH_2.CO_2.C_7H_5O + H_2O = CH_2.NH_2.CO_2.H + C_6H_5.CO_2.H$.

Hippuric acid crystallises in rhombic prisms, sparingly soluble in cold water, soluble in hot water and in alcohol, but insoluble in ether, which distinguishes it from benzoic acid. Like benzoic, it dissolves easily in ammonia, and is precipitated, in feathery crystals, by hydrochloric acid; but these are not dissolved on adding ether.

The more complex character of hippuric acid is shown by the action of heat, for whereas benzoic acid sublimes without decomposition, hippuric assumes a red colour, gives a small sublimate of benzoic acid, and evolves hydrocyanic acid, *benzamide*, $C_7H_5O.NH_2$, and *benzonitrile*, or *phenyl cyanide*, $C_6H_5.CN$, which smells of bitter almonds.

The *hippurates* resemble the benzoates; in solution, they give a buff precipitate with ferric chloride.

401. *Uric acid*, or *lithic acid*, $C_5H_4N_4O_3$, or $C_2(CO)_3(NH)_4$.—Uric acid is generally prepared from the excrement of the boa-constrictor (*serpent's urine* from the Zoological Gardens), which consists chiefly of *hydro-ammonium urate*, $H.NH_4.C_5H_2N_4O_3$; this is dissolved by boiling with dilute potash, which expels NH_3, and converts it into normal *potassium urate*, $K_2C_5H_2N_4O_3$; by passing CO_2 through this, the sparingly soluble *hydropotassium urate*, $HKC_5H_2N_4O_3$, is precipitated; this is washed, dissolved in hot water, and decomposed by HCl, which precipitates the uric acid. Human urine also yields uric acid in small crystals when concentrated by evaporation, mixed hot with a little HCl, and set aside; the crystals are much tinged with urinary colouring matter, and may be purified by dissolving in potash and treating as above; healthy urine yields, at most, one-thousandth, by weight, of the acid.

Guano, the partly decomposed excrement of sea-birds, contains much uric acid, which may be extracted from it by boiling with a 5 per cent. solution of borax, and adding HCl to the filtered solution.

Uric acid is a white crystalline powder, appearing under the microscope in peculiar modifications of the rhombic prism. It is very sparingly soluble in water, requiring 1800 parts of boiling water and 14,000 parts of cold water; and it is insoluble in alcohol and ether, but dissolves in glycerin and in alkaline liquids. When heated, it is carbonised and decomposed, emitting odours of ammonia and hydrocyanic acid; urea, $CO(NH_2)_2$, and cyanuric acid, $C_3N_3H_3O_3$, are also found among the products. Strong sulphuric acid, heated with uric acid, dissolves it without blackening, and, on cooling, deposits crystals containing two molecules of sulphuric acid; water separates uric acid from them. Nitric acid dissolves uric acid easily when gently warmed, effervescence taking place from escape of nitrogen, CO_2, and oxides of nitrogen. On evaporating the solution, it leaves a yellow residue, which becomes red when further heated. This residue is a mixture of several products of oxidation of uric acid, and assumes fine purple colours when treated with ammonia or potash (*murexide test*). Uric acid acts as a reducing agent; it precipitates cuprous oxide from alkaline cupric solutions, and reduces silver nitrate to the metallic state if a little sodium carbonate is added.

When uric acid is heated with strong hydriodic acid in a sealed tube to 160°–170° C., it yields glycocine, and the products of decomposition of urea, viz., NH_3 and CO_2. Conversely, if glycocine be heated with excess of urea to 230°, uric acid is formed—

$$\underset{\textbf{Glycocine.}}{CH_2NH_2.CO_2H} + \underset{\textbf{3 mols. urea.}}{3CO(NH_2)_2} = \underset{\textbf{Uric acid.}}{C_2(CO)_3(NH)_4} + 3NH_3 + 2H_2O.$$

Urea is found among the products of distillation and oxidation of uric acid.

The acid character of uric acid is feeble, and its salts are, for the most part, sparingly soluble; it is dibasic. *Hydrosodium urate*, $HNaC_5H_2N_4O_3$, occurs in the gouty concretions termed *chalk-stones*, and sometimes as a deposit from urine.

The hydro-ammonium urate is the buff or pink deposit so often formed in urine on cooling; it disappears on gently warming; the colour does not belong to the salt itself. *Hydrolithium urate*, $HLi\bar{U}$, is the most soluble urate, requiring 370 parts of cold and 40 parts of boiling water, whilst the sodium salt requires 1100 parts cold and 124 parts boiling, and the ammonium salt requires 1600 parts of cold water.

Uric acid and urates are very common constituents of urinary calculi. They are also found in minute quantity in blood and some other animal fluids, and in the solid parts of some animals.

When uric acid is added by degrees to strong nitric acid, it dissolves with effervescence, caused by liberation of CO_2 and N, and the liquid becomes hot. On cooling, it deposits octahedral crystals of *alloxan*, $C_3O_3(NH)_2CO$, or *mesoxalyl-urea*, which stains the skin pink, and gives an intense purple colour with ferrous sulphate and a trace of potash. The octahedral crystals contain 1Aq, but it may be crystallised in prisms with 4Aq.

When alloxan is boiled with baryta water, it deposits a crystalline precipitate, which is the barium salt of *alloxanic acid*—

$$C_3O_3(NH)_2CO + H_2O = NH_2.CO.NH(CO)_2.CO.OH.$$

If the boiling be long continued, the products are urea and the barium salt of *mesoxalic acid*—

$$NH_2.CO.NH(CO)_2.CO.OH + HOH = \underset{\textit{Urea.}}{CO(NH_2)_2} + \underset{\textit{Mesoxalic acid.}}{CO(CO.OH)_2}$$

Nascent hydrogen converts mesoxalic into tartronic acid; $CO(CO_2H)_2 + H_2 = CH.OH(CO_2H)_2$ (*tartronic acid*). Uric acid may be represented as derived from tartronic acid and urea by the abstraction of 4 molecules of water—

$$CH.OH(CO_2H)_2 + 2CO(NH_2)_2 \text{ (\textit{urea})} = 4H_2O + C_2.CO.2CO(NH)_2 \text{ (\textit{uric acid})}.$$

This would indicate uric acid to be the *di-ureide of tartronic acid*. By hydrogenising alloxan, it is converted into *dialuric acid*, or *tartronyl-urea*, $CO.N_2H_2(C_3H_2O_3)''$. This is effected by passing H_2S through a boiling solution of alloxan, when sulphur is precipitated. Dialuric acid crystallises in needles, which absorb oxygen when exposed to air, and are converted into *alloxantin*, $C_8H_4N_4O_7$.

$$2(CO.N_2H_2.C_3H_2O_3) + O = 2H_2O + (CO)_2.N_4(C_3H_2O_2)_2O \ (\textit{alloxantin}).$$

This body is also precipitated, together with sulphur, when H_2S is passed into a cold solution of alloxan, when the dialuric acid formed at first reacts with the excess of alloxan, and the alloxantin, being nearly insoluble in cold water, is removed from the further action of the H_2S.

Alloxantin is precipitated on mixing solutions of alloxan and dialuric acid—

$$\underset{\textit{Alloxan.}}{C_3O_3(NH)_2CO} + \underset{\textit{Dialuric acid.}}{CO.N_2H_2.C_3H_2O_3} = H_2O + \underset{\textit{Alloxantin.}}{(CO)_2.N_4(C_3H_2O_2)_2O}$$

When uric acid is dissolved in hot dilute nitric acid, alloxantin is the chief product, and its preparation may be combined with that of alloxan by treating the cooled mother-liquor from the alloxan with H_2S, and boiling the precipitate with water, which extracts the alloxantin and deposits it, on cooling, in prisms containing 3Aq. It has an acid reaction, and produces a fine violet precipitate with baryta-water, which is bleached by boiling, being converted into the alloxanate and dialurate. Ferric chloride and a trace of ammonia give a blue colour with alloxantin. It becomes red when exposed to air containing ammonia. On adding ammonium chloride to a hot saturated solution of alloxantin, it becomes first purple and then colourless, depositing a crystalline precipitate of *uramil*, and leaving alloxan in solution; $(CO)_2(N_2C_3H_2O_2)_2O$ (*alloxantin*) + $NH_3.HCl = HCl + C_3O_3(NH)_2CO$ (alloxan) + $C_4H_3.NH_2.N_2O_3$ (*uramil*, also called *murexan* and *dialuramide*). If an ammoniacal solution of uramil be mixed with an ammoniacal solution of alloxan, a purple solution is formed which deposits crystals, with a green metallic lustre, of *murexide*, or *acid ammonium purpurate*, $NH_4.C_8H_4N_5O_6.H_2O$, the constitution of which is uncertain, but the formula is the sum of one molecule of uramil, one of alloxan, and one of ammonia. Since alloxan and uramil are both produced when uric acid is evaporated with nitric acid, it is easy to account for the purple colour produced by treating the residue with ammonia.

Murexide is also formed by heating alloxantin to 100° C. in a current of ammonia-gas, when water is eliminated—

$$\underset{\textit{Alloxantin.}}{(CO)_2(N_2C_3H_2O_2)_2O} + 2NH_3 = H_2O + \underset{\textit{Murexide.}}{(CO)_2(N_2C_3H_2O_2)_2(NH_2)_2}$$

When uramil is boiled with water and mercuric oxide, an atom of oxygen from the latter acts upon 2 molecules of uramil, yielding murexide and water. Crystals of murexide are also obtained by dissolving 7 parts of (prismatic) alloxan and 4 parts of alloxantin in 240 parts of hot water, and adding 80 parts of a cold saturated solution of ammonium carbonate. Murexide is sparingly soluble in cold water, and insoluble in alcohol and ether. Potash dissolves it with a rich purple colour. Acids bleach it, apparently producing uramil.

When alloxantin is heated with strong sulphuric acid, at 100° C., as long as SO_2 is evolved, it is converted into *barbituric acid*, or *malonyl-urea*, $CO.N_2H_2(C_3H_2O_2)''$, which is also obtained synthetically by heating urea with malonic acid and phosphorus oxychloride—

$$3CH_2(CO.OH)_2 + 3CO(NH_2)_2 + 2POCl_3 = 3(CO.N_2H_2.C_3H_2O_2) + 2PO(OH)_3 + 6HCl.$$

Barbituric acid is sparingly soluble in cold water. When boiled with alkalies, it yields malonic acid and urea. *Amido-barbituric acid*, or *amido-malonyl-urea*, $CO.N_2H_2.C_3H.NH_2.O_2$, is identical with uramil.

Parabanic acid, or *oxalyl-urea*, $CO.N_2H_2(C_2O_2)''$, is the chief product of the more violent oxidation of uric acid, and is prepared by gradually adding uric acid to six parts of nitric acid (sp. gr. 1.3) at 70° C., evaporating to dryness on the steam-bath, and recrystallising from water. It forms prisms which are strongly acid, dissolve in alcohol, but not in ether. It is a dibasic acid; its solution gives, with silver nitrate, a characteristic crystalline precipitate of $CO.N_2Ag_2(C_2O_2).H_2O$. When boiled with dilute acids, parabanic acid yields urea and oxalic acid, and it may be synthesised from these substances in the presence of phosphorous oxychloride; $(CO.OH)_2 + CO.N_2H_4 = 2HOH + CO.N_2H_2.C_2O_2$. Most oxidising agents convert uric into parabanic acid; *e.g.*, bromine and water, HCl and potassium chlorate, MnO_2 and H_2SO_4.

Oxaluric acid, $NH_2.CO.NH.CO.CO.OH$ or $CO.N_2H_3.HO.C_2O_2$, is formed by the action of alkalies on parabanic acid, when it combines with the elements of water; $CO.N_2H_2.C_2O_2 + H_2O = CO.N_2H_3.HO.C_2O_2$. Ammonia is preferable, because potash decomposes the product. When parabanic acid is boiled with ammonia, ammonium oxalurate crystallises in needles after cooling. If these be dissolved in hot water, HCl precipitates oxaluric acid as a crystalline powder. This acid has the same relation to parabanic acid as alloxanic acid has to alloxan—

Alloxan . .	$N_2H_2(CO)_4$	Parabanic acid .	$N_2H_2(CO)_3$
Alloxanic acid .	$N_2H_3(CO)_3.CO_2H$	Oxaluric acid . .	$N_2H_3(CO)_2.CO_2H$

A small quantity of ammonium oxalurate may be extracted from urine by animal charcoal, which, after having served for the filtration of a large volume of urine, is well washed with water, and boiled with alcohol, which leaves the oxalurate mixed with colouring matter, when evaporated.

Oxaluramide, $N_2H_3(CO)_2.CO.NH_2$, is metameric with *ammonium parabanate*, $CO.N_2H.NH_4.C_2O_2$, and is obtained by heating that salt to 100° C.

Dimethyl-parabanic acid, $CO.N_2(CH_3)_2.C_2O_2$, or *cholestrophane*, is formed when silver parabanate is heated with methyl iodide. It is interesting from having been originally obtained by the oxidation of caffeine (see *Caffeine*).

The principal immediate products of the oxidation of uric acid in acid solution have been seen to be alloxan, parabanic acid, and urea, but when an alkaline solution of uric acid in potash is exposed to air, it slowly absorbs oxygen and deposits crystals of the potassium salt of *uroxanic acid*, from which the acid may be precipitated by HCl—

$$C_5H_4N_4O_3 \text{ (\textit{uric acid})} + 2H_2O + O = C_3H_6N_4O_2(CO_2H)_2 \text{ (\textit{uroxanic acid})}.$$

When boiled with water, it is decomposed into single molecules of CO_2, urea, and *glyoxyl-urea*, $CO.N_2H_3(C_2HO_2)$, or *allanturic acid.*

When uric acid is boiled with lead dioxide and water, a precipitate of lead oxalate is formed, and the filtered liquid deposits crystals of *allantoin*, while the mother-liquor yields urea on evaporation; $2C_5H_4N_4O_3$ (*uric acid*) $+ O_2 + 5H_2O = C_4H_6N_4O_3$ (*allantoin*) $+ 2CON_2H_4$ (*urea*) $+ 2C_2H_2O_4$ (*oxalic acid*). Allantoin is found in the allantoic liquid of the calf.

Iso-uric acid, having the same composition as uric acid, is deposited on boiling solution of alloxantin with solution of cyanamide. It is more easily oxidised than uric acid—

$$C_8H_4N_4O_7 \text{ (\textit{alloxantin})} + 2(CN.NH_2) \text{ (\textit{cyanamide})} = 2C_5H_4N_4O_3 \text{ (\textit{iso-uric acid})} + O.$$

Some alloxan is formed at the same time by the oxidation of some of the alloxantin.

The subjoined formulæ, though not expressing, in all cases, the true constitution of uric acid and its chief derivatives, may be found useful in assisting the memory:—

Uric acid	$(CO.N_2H_2)_2C(C_2O_2)$
Urea	$CO.N_2H_4$
Oxalyl-urea, or parabanic acid . .	$CO.N_2H_2(C_2O_2)$
Mesoxalyl-urea, or alloxan . . .	$CO.N_2H_2(C_3O_3)$
Malonyl-urea, or barbituric acid . .	$CO.N_2H_2(C_3H_2O_2)$
Tartronyl-urea, or dialuric acid . .	$CO.N_2H_2(C_3H_2O_3)$
Glyoxyl-urea, or allanturic acid . .	$CO.N_2H_3(C_2HO_2)$
Amido-malonyl-urea, or uramil . .	$CO.N_2H_2(C_3H.NH_2.O_2)$
Oxaluric acid	$CO.N_2H_2(C_2H_2O_3)$
Alloxanic acid	$CO.N_2H_2(C_3H_2O_4)$
Alloxantin	$(CO)_2.N_4(C_3H_2O_2)_2O$
Murexide	$(CO)_2.N_4(C_3H_2O_2)_2(NH_2)_2$

402. Ketones or Acetones.—The ketones are formed from the acids by removing the OH from the group CO.OH, characteristic of the acids, and replacing it by another radical, usually one of the hydrocarbon radicals of the alcohols; thus, if OH be removed from acetic acid, $CH_3.CO.OH$, and replaced by methyl, CH_3, the result will be *acetone*, $CH_3.CO.CH_3$. The ketones, therefore, contain the group CO, or carbonyl, which is also present in the aldehyds; and it will be seen, on studying the constitution of the alcohols, that the ketones are

really the aldehyds of a particular class of alcohols, called, from their internal structure, *secondary alcohols*, and that these may be converted into ketones by partial oxidation, just as alcohol is converted into aldehyd, whilst the ketones yield secondary alcohols with nascent hydrogen, just as aldehyd yields alcohol.

It was shown at page 501 that the aldehyd of any acid could generally be obtained by distilling a mixture of a salt of that acid with a formate; thus, a mixture of potassium acetate with potassium formate would yield acetic aldehyd; $CH_3.CO.OK + H.CO.OK = CH_3.CO.H + OK.CO.OK$. The salts of the alkali-metals, by reason of their stability, are not so fitted for this reaction as the calcium salts. If calcium acetate be distilled with calcium formate, acetic aldehyd would be produced according to the equation—

$$(CH_3.CO.O)_2Ca + (H.CO.O)_2Ca = 2(CH_3.CO.H) + 2(Ca.CO.O_2).$$

But if calcium acetate be distilled with calcium acetate, that is, by itself, the products will be acetone and calcium carbonate—

$$(CH_3.CO.O)_2Ca + (CH_3.CO.O)_2Ca = 2(CH_3.CO.CH_3) + 2(Ca.CO.O_2).$$

The aldehyds contain an atom of hydrogen united to an alcohol-radical by the mediation of the CO group, whilst the ketones contain two alcohol radicals united through the CO group. If these radicals be different, a *double ketone* is the result; thus, by distilling a mixture of calcium acetate and calcium propylate, *acetone-propione* is obtained—

$$(CH_3.CO.O)_2Ca + (C_2H_5.CO.O)_2Ca = 2(CH_3.CO.C_2H_5) + 2(Ca.CO.O_2).$$

When acted on by oxidising agents, the ketones yield two acids, whilst the aldehyds yield only one, since the former contain two hydrocarbon radicals. Thus, acetone, $CH_3.CO.CH_3$, yields formic acid, $H.CO.OH$, and acetic acid, $CH_3.CO.OH$; propione, $C_2H_5.CO.C_2H_5$, yields acetic acid and propylic acid, $C_2H_5.CO.OH$. The ketones of the acetic series all yield acetic acid as one of the acids produced by their oxidation, showing that these ketones all contain the group CH_3.

403. *Acetone*, or *dimethyl-ketone*, $CH_3.CO.CH_3$, or *pyro-acetic spirit*, is obtained among the products of distillation of wood (p. 491), and may be prepared by distilling the acetate of lead, calcium, or barium, the last yielding the purest product (see the above equation). The crude distillate is shaken with a saturated solution of hydrosodium sulphite, which combines with acetone (as with aldehyd) to form a crystalline compound, $(CH_3)_2CO.HNaSO_3$. This is freed from the mother-liquor and distilled with sodium carbonate, when acetone distils over mixed with water, which is removed by fused calcium chloride.

Acetone is a colourless fragrant liquid, of sp. gr. 0.81, and boiling at 56°.3 C. It is inflammable, burning with a luminous flame. It mixes with water, alcohol, and ether. On adding solid KHO to its aqueous solution, the acetone separates and rises to the surface. It is a good solvent for certain resins and camphors. It is not so powerful a reducing agent as aldehyd, and does not reduce silver nitrate. When oxidised by potassium permanganate or by dichromate and sulphuric acid, it yields acetic and carbonic acids—

$$CH_3.CO.CH_3 + O_4 = CH_3.CO.OH + CO(OH)_2.$$

Formic acid, $H.CO.OH$, is obtained at an intermediate stage, and afterwards oxidised to carbonic.

When acetone is dissolved in water and acted on by amalgam of sodium, the nascent hydrogen converts it into two alcohols, the *isopropylic*, having the same composition as propylic, $C_3H_7.OH$, and a crystalline alcohol termed *pinacone*, $(CH_3)_4C_2(OH)_2$; $3(CH_3.CO.CH_3) + H_4 = CH_3.CH.OH.CH_3 + (CH_3)_2C_2(OH)_2(CH_3)_2$. The constitution of these alcohols will be studied hereafter.

Acetone has been produced synthetically by the action of zinc methide on acetyl chloride; $2(CH_3.COCl) + Zn(CH_3)_2 = ZnCl_2 + 2(CH_3.CO.CH_3)$. It is also formed when vapour of acetic acid is passed through a red-hot tube, and when starch, sugar, and many other organic bodies undergo destructive distillation. It occurs in the urine of diabetic patients.

When acted on by dehydrating agents, such as sulphuric or hydrochloric acid or quicklime, acetone loses the elements of water, and yields *condensation-products*, richer in carbon; thus, two molecules of $(CH_3)_2CO$, losing H_2O, give $C_6H_{10}O$, *mesityl oxide*, a liquid smelling of peppermint, and boiling at 130° C. Three molecules of $(CH_3)_2CO$, losing $2H_2O$, yield $C_9H_{14}O$, *phorone*, a crystalline solid, smelling of geraniums, and boiling at 190°, whilst the loss of another H_2O gives C_9H_{12}, *mesitylene*, a liquid boiling at 163°.

Metacetone, $C_6H_{10}O$, obtained by distilling sugar with lime, is isomeric with mesityl oxide, and boils at 84° C.

404. The following table enumerates the principal ketones; none of them, except acetone, has at present any practical application.

Ketone.	Formula.	Boiling Point C.
Dimethyl	$CH_3.\ CO.CH_3$	56°
Methyl-ethyl	$CH_3.\ CO.C_2H_5$	81
Propione	$C_2H_5.\ CO.C_2H_5$	100
Methyl-propyl	$CH_3.\ CO.C_3H_7$	101
Methyl-butyl	$CH_3.\ CO.C_4H_9$	127
Propyl-ethyl	$C_3H_7.\ CO.C_2H_5$	128
Methyl-amyl	$CH_3.\ CO.C_5H_{11}$	155
Butyrone	$C_3H_7.\ CO.C_3H_7$	144
Valerone	$C_4H_9.\ CO.C_4H_9$	181
Caprone	$C_5H_{11}.CO.C_5H_{11}$	220
Benzophenone	$C_6H_5.\ CO.C_6H_5$	...
Acetophenone	$CH_3.\ CO.C_6H_5$	199

From their constitution, the ketones must afford many cases of isomerism: thus, propione and methyl-propyl ketone have the same ultimate composition; so have methyl-butyl and propyl-ethyl ketones; methyl-amyl ketone and butyrone form another pair. Moreover, each ketone of the acetic series is isomeric with the aldehyd of the acid following next in the series: thus, acetic ketone, $(CH_3)_2CO$, is isomeric with propylic aldehyd, $C_2H_5.CO.H$; propione, $(C_2H_5)_2CO$, is isomeric with valeric aldehyd, $C_4H_9.CO.H$.

Methyl-ethyl ketone may be obtained by the reaction between acetyl chloride and zinc ethide; $2(CH_3.COCl) + Zn(C_2H_5)_2 = 2(CH_3.CO.C_2H_5) + ZnCl_2$. It is present in small proportion in commercial acetone. When oxidised, it yields only one acid, acetic; $CH_3.CO.C_2H_5 + O_3 = 2(CH_3.CO.OH)$.

Propione is obtained by distilling calcium propylate—

$$(C_2H_5CO_2)_2Ca \;=\; C_2H_5.CO.C_2H_5 \;+\; CaCO_3;$$

also by the action of propyl chloride on zinc ethide; $2(C_2H_5.COCl) + Zn(C_2H_5)_2 = 2(C_2H_5.CO.C_2H_5) + ZnCl_2$. It is also formed when zinc ethide is decomposed by potassium, and the resulting compound of zinc ethide and potassium ethide is acted on by carbonic oxide; $2KC_2H_5 + CO = C_2H_5.CO.C_2H_5 + K_2$. Propione does not combine with hydrosodium sulphite. When oxidised, it yields acetic and propylic acids.

Methyl-nonyl ketone, $CH_3.CO.C_9H_{19}$, is the chief constituent of *oil of rue*, from which it may be precipitated by hydrosodium sulphite. It may be obtained artificially by distilling calcium acetate with calcium rutate.

Naphthyl-phenyl ketone, $C_{10}H_7.CO.C_6H_5$, forms a dibromide, which is useful in optical experiments, on account of its high refractive power.

405. ETHERS.—The ethers are derived from the alcohols by the substitution of an alcohol-radical for the hydrogen in the hydroxyl group; thus, if methyl alcohol, $CH_3.OH$, be treated with sodium, the hydroxyl hydrogen is displaced by sodium, and $CH_3.ONa$, or *sodium methylate*, is obtained. If this be acted on by methyl iodide—

$$CH_3.ONa \;+\; CH_3I \;=\; CH_3.O.CH_3 \;+\; NaI;$$

the H in CH_3OH has been displaced by CH_3, and *methyl ether*, $CH_3.O.CH_3$, has been formed. It will be evident that a similar reaction between sodium methylate and ethyl iodide, C_2H_5I, would furnish methyl-ethyl ether, $CH_3.O.C_2H_5$, so that the number of ethers obtainable would exceed that of the alcohols.

The ethers are generally insoluble in water, and lighter and more volatile than the corresponding alcohols. They are not, as a rule, so easily acted on by other bodies as the alcohols are. When oxidised, they yield aldehyds and acids. They are generally convertible into alcohols by the action of water at high temperatures, the H_2O exchanging H for one of the alcohol-radicals. With hydrogen haloid acids, especially with hydriodic acid, they yield haloid compounds, imitating, though with much less energy, the reactions of those acids with the alkaline oxides, such as K_2O, which resemble the ethers in constitution; thus—

$$K_2O + 2HI = H_2O + 2KI; \text{ and } (CH_3)_2O + 2HI = H_2O + 2CH_3I.$$

406. *Ether*, or *sulphuric ether*, $C_2H_5.O.C_2H_5$, is prepared by distilling alcohol with sulphuric acid. If two measures of alcohol be carefully added to one measure of strong sulphuric acid, and the mixture distilled, ether passes over together with water, and if alcohol be added from time to time, a small quantity of sulphuric acid suffices to etherify a large quantity of alcohol. The alcohol is first converted into hydroethyl sulphate, or *sulphethylic acid*—

$$H_2SO_4 + C_2H_5.OH = HC_2H_5SO_4 + HOH.$$

When this is heated to about 140° C. with more alcohol, it is decomposed into ether and sulphuric acid, which then acts in the same way upon a fresh quantity of alcohol—

$$HC_2H_5SO_4 + C_2H_5.OH = C_2H_5.O.C_2H_5 + H_2SO_4.$$

Hence the process has been termed the continuous etherifying process, and is carried out in the following manner:—Alcohol of sp. gr. 0.83 is carefully added, with continued shaking, to an equal volume of strong sulphuric acid, cooled in a vessel of water. When the mixture has cooled, it is poured into a retort or flask (fig. 280), which is connected with a reservoir of alcohol and a well-cooled condenser. The mixture

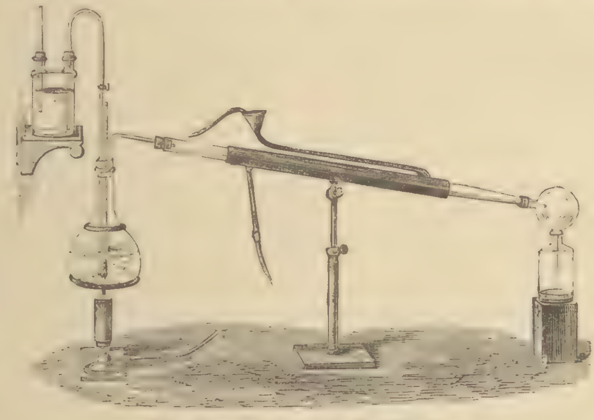

Fig. 280.—Continuous etherification.

is quickly heated till it boils, when its temperature will be about 140° C. (284° F.), and alcohol is then allowed to pass in slowly from a siphon tube furnished with a stop-cock, and dipping below the liquid in the flask; the rate of flow of the alcohol is so regulated as to keep the mixture at the same level, in order that its temperature may remain as nearly as possible at 140° C. This is rendered easier if a thermometer be fixed in the cork with its bulb in the liquid. When the total quantity of alcohol used amounts to six or seven times that originally taken, the process must be stopped, because secondary reactions, attended by carbonisation, have used up much of the sulphuric acid. The liquid collected in the receiver contains about two-thirds of its weight of ether, with about one-sixth of water, and an equal quantity of alcohol, and a little sulphurous acid. It usually separates into two layers, of which the upper is ether. The whole is introduced into a narrow stoppered bottle, and shaken with cold water, added in small portions, as long as the layer of ether on the surface increases in volume; a little potash is then added, and, after shaking, the upper layer of ether is drawn off, by a siphon or separator, into a flask containing lumps of fused calcium chloride, to remove water and alcohol. After standing for some hours, the ether is distilled off in a water-bath at as low a temperature as possible. To free it entirely from water, it must be again rectified after digestion with powdered quick-lime, and finally with bright sodium till no more hydrogen bubbles are visible. *Methylated ether* is prepared from *methylated spirit*, and is much cheaper than pure ether, for which it may often be substituted.

Theory of etherification.—The process described above for the preparation of ether had long been practised before a satisfactory explanation of it was arrived at. One of the earliest views regarded the formation of ether as a simple removal of water by the sulphuric acid from the alcohol, which was then believed to be a compound of ether and water; but against this it was urged that the water was not retained by the acid, but distilled over with the ether, and that the same acid would etherify successive additions of alcohol. Passing over the theory of *catalytic* action, or decomposition by contact, which was a mere statement of the facts without any real explanation, we come to the important observation that the first product of the action of sulphuric acid on alcohol is sulphethylic acid, which is decomposed, when distilled with more alcohol at 140°, into ether, water, and sulphuric acid, as in the equations given on p. 547. Very strong evidence in favour of this view is furnished by the following experiment:—Amyl alcohol, $C_5H_{11}.OH$, is converted by sulphuric acid into *sulphamylic acid*, $C_5H_{11}.SO_4H$, which is heated in the flask (fig. 280), whilst ethyl alcohol, $C_2H_5.OH$, is allowed to flow in from the reservoir; this decomposes the sulphamylic acid, yielding sulphuric acid and *amyl-ethyl ether*—

$$C_5H_{11}.SO_4H + C_2H_5.OH = C_5H_{11}.O.C_2H_5 + H_2SO_4.$$

If the process is continued after all the amyl-ethyl ether has passed over, only ethyl ether is obtained.

Properties of ether.—A very mobile colourless liquid with a characteristic odour; sp. gr., at 15° C., 0.70. It boils at 34°.9 C., evaporates very rapidly in air, producing intense cold, and yielding a very heavy vapour, of sp. gr. 2.59, which is very inflammable, and renders ether dangerous in unskilled hands. It is sparingly soluble in water, so that, when shaken with it, the ether generally rises to the surface on standing, rendering it very useful for collecting certain substances, such as bromine and alkaloids, from large bulks of aqueous solutions into a small bulk of ether. Ten volumes of water dissolve one volume of ether. Thirty-four volumes of ether are required to dissolve one volume of water, so that ether free from alcohol could not contain much water, but commercial ether contains alcohol, which enables it to take up a larger quantity of water. Ether and alcohol may be mixed in all proportions, but the addition of much water generally brings the ether to the surface. Ether has been solidified to a crystalline mass at −129° C. Ether is much used in laboratories as a solvent, especially for fatty substances and alkaloids, and by the photographer in making collodion.

The properties of ether admit of some interesting experiments.

1. If a little ether be evaporated by blowing upon it in a watch-glass, with a drop of water hanging from its convexity, the water will be speedily frozen. A thin beaker containing ether may be frozen to a wet table by blowing into it with the bellows.

2. A piece of tow, wool, or sponge, wetted with ether, is placed at the upper end of a sloping trough or gutter of wood or metal, over six feet long; a match applied at the lower end fires the train of vapour.

3. A jug is warmed with a little hot water, emptied, and a little ether poured into it; the vapour may be poured into a row of small beaker glasses, each of which is afterwards tested with a taper.

4. A pneumatic trough is filled with warm water, and a small test-tube filled with ether is inverted with its mouth under the water, and quickly decanted up into a gas-jar filled with warm water, when it will be vaporised, and may be decanted through the water into other vessels and treated like a permanent gas. Some cold water poured over the jar containing it at once proves its condensible character.

407. Ether is produced by other reactions than that between alcohol and sulphuric acid, and although these are not used for the economical preparation of ether, they explain its constitution and confirm the modern view of etherification. Thus, ethyl iodide heated with disodium oxide, in a sealed tube, to 180° C., yields ether and sodium iodide; $2C_2H_5I + Na_2O = (C_2H_5)_2O + 2NaI$. Silver oxide, Ag_2O, effects the conversion more easily. Alcohol heated with ethyl bromide and potash yields ether, water, and potassium bromide; $C_2H_5.OH + C_2H_5Br + KOH = (C_2H_5)_2O + HOH + KBr$. Ethyl iodide acted on by sodium ethylate yields ether and sodium iodide; $C_2H_5I + C_2H_5.ONa = C_2H_5.O.C_2H_5 + NaI$. Ethyl iodide heated with a small quantity of water, under pressure, yields, first alcohol, and afterwards ether—

$$C_2H_5I + HOH = C_2H_5.OH + HI, \text{ and } C_2H_5I + C_2H_5.OH = C_2H_5.O.C_2H_5 + HI.$$

Other acids beside sulphuric are able to produce ether from alcohol, especially those which are non-volatile and polybasic, such as phosphoric, arsenic, and boracic, which probably act in the same way as sulphuric. But certain salts, such as zinc chloride and aluminium sulphate, also generate ether from alcohol, and the explanation of this is less simple. It will be found that such salts are capable of decomposition by water, with formation of basic salts, and free acid; thus, $ZnCl_2 + HOH = ZnCl.OH + HCl$, or $Al_2(SO_4)_3 + 4HOH = Al_2SO_4(OH)_4 + 2H_2SO_4$. If these reactions take place with alcohol, $C_2H_5.OH$, instead of with HOH, the products would be C_2H_5Cl instead of HCl, and $C_2H_5.HSO_4$ instead of H_2SO_4, and it has been seen that either of these would react with the excess of alcohol to produce ether.

Ether may be converted into alcohol by heating it with water and a very little sulphuric acid, in a sealed tube, to 180° C. The ether is probably converted at first into sulphethylic acid; $(C_2H_5)_2O + 2H_2SO_4 = 2(C_2H_5.HSO_4) + H_2O$; and sulphethylic acid heated with much water yields alcohol and sulphuric acid—

$$C_2H_5.HSO_4 + HOH = C_2H_5.OH + H_2SO_4.$$

When ether is acted on by hydriodic acid gas, in the cold, it yields alcohol and ethyl iodide; $(C_2H_5)_2O + HI = C_2H_5.OH + C_2H_5I$.

If a *mixed* ether, such as ethyl-amyl ether, be treated in this way, the radical containing most carbon is the one converted into an alcohol; $C_2H_5.O.C_5H_{11} + HI = C_5H_{11}.OH + C_2H_5I$.

Ordinary oxidising agents convert ether into aldehyd and acetic acid. Ozonised oxygen converts it into formic, acetic, and oxalic acids and hydric peroxide.

When ether-vapour is passed over heated potash; hydrogen, marsh gas, and potassium carbonate are formed, potassium acetate being probably formed in the first stage of the reaction; $(C_2H_5)_2O + 2KHO + H_2O = 2KC_2H_3O_2 + 4H_2$.

Ether enters into combination with several metallic chlorides and bromides, forming crystalline compounds; stannic chloride combines with two molecules of ether, forming $SnCl_4(C_4H_{10}O)_2$; aluminium bromide forms $Al_2Br_6(C_4H_{10}O)_2$.

Ether is inflamed by contact with chlorine; but if it be very well cooled, and light be excluded, it yields a series of substitution-products—

Monochlorether, C_4H_9ClO, boiling at 98° C.

Dichlorether, $C_4H_8Cl_2O$, boiling at 140°.

Tetrach'orether, $C_4H_6Cl_4O$, decomposed by heat.

Perchlorinated ether, $C_4Cl_{10}O$, requiring sunlight for its formation; a crystalline body smelling like camphor.

408. *Methylic ether*, or *dimethyl oxide*, $CH_3.O.CH_3$, is a *gas* prepared by adding methyl-alcohol (2 parts by weight) to cooled sulphuric acid (3 parts) and heating to about 140° C., keeping up a supply of methyl-alcohol, as in the preparation of ether. The reaction is the same as in the preparation of ether, hydromethyl sulphate, or *sulphomethylic acid*, $CH_3.HSO_4$, being formed at first, and decomposed by more methyl-alcohol. The gas may be stored for use by passing it into cooled H_2SO_4, which dissolves 600 volumes of it and gives it up again when mixed with water.

Methyl-ether is a fragrant gas, condensed by cold or pressure to a liquid boiling at −21° C., and used for producing cold. Water absorbs about 37 times its volume of the gas. It is inflammable.

Methyl-ethyl ether, $CH_3.O.C_2H_5$, is also a gas at the ordinary temperature, obtained by distilling a mixture of methyl-alcohol and ethyl-alcohol with sulphuric acid. By cold or pressure it may be condensed to a liquid boiling at 11° C. Ethers containing, like this, two alcohol radicals are called *mixed ethers*.

Propylic ether, or *dipropyl oxide*, $C_3H_7.O.C_3H_7$, is obtained by heating propyl iodide with potash and propyl-alcohol—

$$C_3H_7I + KHO + C_3H_7.OH = C_3H_7.O.C_3H_7 + KI + HOH.$$

It boils at 86° C.

Methyl-propyl ether, $CH_3.O.C_3H_7$, metameric with ethyl ether, boils at about 50°.

Ethyl-propyl ether, $C_2H_5.O.C_3H_7$, boils at about 85°.

Butyl ether, $C_4H_9.O.C_4H_9$, boils at 140°.

Butyl-ethyl ether, $C_4H_9.O.C_2H_5$, boils at 92°.

Cetyl ether, $C_{16}H_{33}.O.C_{16}H_{33}$, is a crystalline solid, fusing at 55° C., and boiling at about 300°.

409. It will be remarked that the ethers derived from the alcohols of the series $C_nH_{2n+2}O$ form an homologous series isologous with the alcohols, that each ether is metameric with the isologous alcohol, and that the ethers containing an odd number of carbon-atoms are mixed ethers.

Ethers.		Alcohols.	
Methylic . . .	$CH_3.O.CH_3$	Ethylic . . .	$C_2H_5.OH$
Methyl-ethylic .	$CH_3.O.C_2H_5$	Propylic . . .	$C_3H_7.OH$
Ethylic . . .	$C_2H_5.O.C_2H_5$	Butylic . . .	$C_4H_9.OH$
Ethyl-propylic .	$C_2H_5.O.C_3H_7$	Amylic . . .	$C_5H_{11}.OH$
Propylic . . .	$C_3H_7.O.C_3H_7$	Caproic . . .	$C_6H_{13}.OH$

410. The dihydric alcohols or glycols also yield ethers when their hydroxyl hydrogen is displaced by a radical. Thus, glycol or ethene alcohol, $C_2H_4(OH)_2$, yields $C_2H_4O_2.C_2H_4$, *di-ethene dioxide*. To obtain this body, glycol is saturated with HCl gas and distilled, when it yields *glycol-chlorhydrin*, or *ethylene hydrate chloride;* $C_2H_4(OH)_2 + HCl = C_2H_4.OH.Cl + HOH$. When this is distilled with potash, it gives ethylene oxide; $C_2H_4.OH.Cl + KHO = C_2H_4O + KCl + H_2O$. When ethylene oxide is treated with bromine, it is converted into $(C_2H_4O)_2Br_2$, from which mercury removes the bromine, leaving $(C_2H_4)_2O_2$. This ethylene ether is a liquid, boiling at 102° C., and miscible with water, alcohol, and ether.

When sodium ethylenate (monosodium glycol), $C_2H_4.O_2.HNa$, is acted on by ethyl iodide, it behaves in a similar way to sodium ethylate, yielding NaI and *monethyl glycol ether*, $C_2H_4.O_2.HC_2H_5$; when potassium acts on this, it displaces hydrogen, forming $C_2H_4.O_2.KC_2H_5$, and if this be treated with ethyl iodide, it gives *di-ethyl glycol ether*, $C_2H_4.O_2.(C_2H_5)_2$, and potassium iodide.

The ethers of the glycols are of no practical interest.

411. *Glycerin ether*, $C_3H_5.O_3.C_3H_5$, represents glycerin, $C_3H_5(OH)_3$, in which glyceryl, C_3H_5, has replaced the three hydrogen atoms of the hydroxyl. It is formed when glycerin is distilled with calcium chloride. It is a colourless inodorous liquid, boiling at about 170° C., and of sp. gr. 1.16; it mixes with water. Its behaviour with hydriodic acid is analogous to that of ethyl ether, for it is converted into glycerin and glyceryl tri-iodide—

$$C_3H_5.O_3.C_3H_5 + 3HI = C_3H_5(OH)_3 + C_3H_5I_3.$$

Ethyl glycerin ether, $C_3H_5(OH)_2OC_2H_5$, *di-ethyl glycerin ether*, $C_3H_5.OH(OC_2H_5)_2$, and *tri-ethyl glycerin ether*, $C_3H_5(OC_2H_5)_3$, have been obtained by methods similar to those which furnish the ethyl-glycol ethers.

Allyl ether, $C_3H_5.O.C_3H_5$, may be obtained from allyl alcohol, $C_3H_5.OH$, by displacing the H by sodium and decomposing the *sodium allylate* by allyl iodide; $C_3H_5.ONa + C_3H_5I = C_3H_5.O.C_3H_5 + NaI$. It boils at 82° C., and does not mix with water; it smells of horse-radish, and is found in small quantity in oil of garlic.

Methyl-allyl ether, $CH_3.O.C_3H_5$, obtained from sodium methylate and allyl iodide, boils at 46° C.

Ethyl-allyl ether, $C_2H_5.O.C_3H_5$, boils at 64° C.

Propargyl ether has not been prepared, but *ethyl-propargyl ether*, $C_2H_5.O.C_3H_3$, is obtained by the action of alcoholic potash on glyceryl tribromide—

$$C_3H_5Br_3 + 3KOH + C_2H_5.OH = C_2H_5.O.C_3H_3 + 3HOH + 3KBr.$$

It has a peculiar odour, and boils at 80°. Its connexion with the propargyl series is shown by its giving a precipitate with silver ammonio-nitrate, and a yellow precipitate with ammoniacal cuprous chloride; these precipitates are $C_2H_5.O.C_3H_2Ag$ and $C_2H_5.O.C_3H_2Cu$. (See *Propargyl alcohol*, p. 498.)

Benzyl ether, $C_7H_7.O.C_7H_7$, is prepared by distilling benzyl alcohol with boric oxide, B_2O_3, which removes the elements of water, $2C_7H_7OH - HOH = C_7H_7.O.C_7H_7$. It is a colourless liquid, not miscible with water, and boiling at above 300° C. By acting on benzyl chloride, C_7H_7Cl, with sodium methylate, *methyl-benzyl ether*, $CH_3.O.C_7H_7$, has been obtained; it boils at 168° C. *Ethyl-benzyl ether*, $C_2H_5.O.C_7H_7$, boils at 185°. The reaction between potassium phenylate, $C_6H_5.OK$, and benzyl chloride yields *phenyl-benzyl ether*, $C_6H_5.O.C_7H_7$, as a crystalline solid, fusing at 39° C., and boiling at 287°.

412. The ethers are enumerated in the subjoined table:—

Ether.	Formula.	Boiling point, C. °.
Methylic	$CH_3.O.CH_3$	−21°
Methyl-ethylic	$CH_3.O.C_2H_5$	11
Ethylic	$C_2H_5.O.C_2H_5$	35
Methyl-propylic	$CH_3.O.C_3H_7$	50
Ethyl-propylic	$C_2H_5.O.C_3H_7$	85
Propylic	$C_3H_7.O.C_3H_7$	86
Ethyl-butylic	$C_2H_5.O.C_4H_9$	92
Butylic	$C_4H_9.O.C_4H_9$	140
Cetylic	$C_{16}H_{33}.O.C_{16}H_{33}$	300
Glycol ether	$C_2H_4.O_2.C_2H_4$	102
Monethyl glycol	$C_2H_4.O_2.HC_2H_5$	127
Di-ethyl glycol	$C_2H_4.O_2.(C_2H_5)_2$	124
Glycerin	$C_3H_5.O_3.C_3H_5$	170
Ethyl glycerin	$C_3H_5(OH)_2.O.C_2H_5$	230
Di-ethyl glycerin	$C_3H_5.OH(OC_2H_5)_2$	191
Tri-ethyl glycerin	$C_3H_5.O_3(C_2H_5)_3$	184
Allyl	$C_3H_5.O.C_3H_5$	82
Methyl-allyl	$CH_3.O.C_3H_5$	46
Ethyl-allyl	$C_2H_5.O.C_3H_5$	64
Ethyl-propargyl	$C_2H_5.O.C_3H_3$	80
Benzylic	$C_7H_7.O.C_7H_7$	300
Methyl-benzylic	$CH_3.O.C_7H_7$	168
Ethyl-benzylic	$C_2H_5.O.C_7H_7$	185
Phenyl-benzylic	$C_6H_5.O.C_7H_7$	287

413. HALOID COMPOUNDS FORMED FROM THE ALCOHOLS BY THE SUBSTITUTION OF A HALOGEN RADICAL FOR HYDROXYL.—These are formed from the alcohols by the replacement of the hydroxyl by one of the radicals capable of forming an acid with hydrogen, viz., chlorine, bromine, iodine, fluorine. Hence they stand in the same relation to the alcohols as the haloid salts of the alkali-metals, such as $NaCl$, bear to the hydroxides, such as $NaHO$; but they are really bodies of a different kind, the halogen element not behaving in the same way as in the mineral salts; thus silver nitrate does not precipitate the chlorine from ethyl chloride, $C_2H_5.Cl$, though it does from sodium chloride.

414. *Methyl chloride*, CH_3Cl, is prepared by passing HCl gas into a boiling solution of zinc chloride in twice its weight of methyl alcohol contained in a flask connected with a reversed condenser. The methyl chloride is evolved as a gas which may be washed with a little water to remove HCl, dried by passing over calcium chloride, and condensed in tubes cooled in a mixture of ice and calcium chloride crystals. The final result is expressed by the equation $CH_3.OH + HCl = CH_3Cl + HOH$. The zinc chloride probably acts in the manner described at page 549. Methyl chloride is a gas of ethereal odour, which is liquefied by a pressure of $2\frac{1}{2}$ atmospheres at 0° C. The liquid boils at −23° C. under atmospheric pressure. Four volumes of the gas are absorbed by water, and 35 volumes by alcohol.

Methyl chloride may also be prepared by distilling methyl alcohol with sodium chloride and sulphuric acid. It is made on a large scale, for use in freezing machines, from the trimethylamine obtained by distilling the refuse of the beet-sugar factories; this is neutralised with hydrochloric acid, and heated to 260° C., when it is decomposed into methyl chloride, trimethylamine, methylamine, and hydrochloric acid; $3N(CH_3)_3HCl = 2CH_3Cl + 2N(CH_3)_3 + NH_2CH_3 + HCl$.

Methyl chloride is very stable; potash decomposes it with difficulty, yielding methyl alcohol and potassium chloride. It is used in the preparation of some of the aniline colours.

Ethyl chloride, or *hydrochloric ether*, C_2H_5Cl, is prepared by passing HCl gas into a boiling solution of fused zinc chloride in twice its weight of alcohol of 95 per cent., as directed above for methyl chloride; $C_2H_5.OH + HCl = C_2H_5Cl + HOH$. The vapour is passed through a little water, then over calcium chloride, into 95 per cent. alcohol kept cool by water. The alcohol absorbs half its weight of ethyl chloride, which may be evolved from it by gently heating, and purified by passing through a little sulphuric acid.

Ethyl chloride condenses to a fragrant liquid of sp. gr. 0.92 and boiling point 12°.5 C. It is sparingly soluble in water. It burns with a bright flame edged with green. Ethyl chloride is formed when olefiant gas and HCl are heated together for some time.

Methyl bromide, CH_3Br, is prepared by acting upon methyl alcohol with phosphorus and bromine—

$$5CH_3OH + Br_5 + P = 5CH_3Br + PO(OH)_3 + HOH.$$

Four parts of methyl alcohol are poured on 1 part of red phosphorus in a well-cooled retort with reversed condenser, and 6 parts of bromine are gradually added. After two or three hours, heat is applied by a water-bath, and the vapour condensed by a freezing mixture. Methyl bromide boils at 4°.5, and smells like chloroform.

Ethyl bromide, or *hydrobromic ether*, C_2H_5Br, may be prepared like methyl bromide, using 16 parts of absolute alcohol, 4 parts of red phosphorus, and 10 parts of bromine. It is a liquid boiling at 39° C.

Methyl iodide, CH_3I, is prepared on the same principle as the bromide, 10 parts of iodine being dissolved in 4 parts of methyl alcohol, and 1 part of red phosphorus added in small portions. After heating in a water-bath for some time, the mixture is distilled. The methyl iodide is the lower layer of the distillate. It has a pleasant smell, sp. gr. 2.29, and boils at 42° C. It mixes with alcohol, but not with water. When kept, it becomes brown from separation of iodine. It is converted into CH_3Cl gas when heated with $HgCl_2$ dissolved in ether. Hydriodic acid, at 150° C., converts it into CH_4. Methyl iodide is used in making aniline dyes.

Ethyl iodide, or *hydriodic ether*, C_2H_5I, is prepared by pouring 5 parts of absolute alcohol on 1 part of red phosphorus in a retort, adding gradually 10 parts of iodine in powder, setting aside for twelve hours, and distilling in a water-bath with a good condenser. Ethyl iodide mixed with alcohol distils over, leaving phosphoric acid in the retort, together with some phosphethylic acid formed by its action on some of the alcohol; $5C_2H_5OH + I_5 + P = 5C_2H_5I + PO(OH)_3 + HOH$. The distillate is shaken, in a stoppered bottle, with about an equal measure of water and enough soda to render it alkaline. The ethyl iodide collects as an oily layer at the bottom; this is separated from the upper layer by a tap-funnel or pipette or siphon, allowed to stand with a little fused calcium chloride in coarse powder, to remove the water, and distilled.

Ethyl iodide has a pleasant smell, sp. gr. 1.93, and boiling point 72° C. It becomes brown when kept, especially in the light, iodine being liberated, and butane formed; $2C_2H_5I = C_4H_{10} + I_2$. Ethyl iodide is sparingly dissolved by water, but readily by alcohol and ether.

Ethyl iodide is a very important reagent in organic researches for introducing the group C_2H_5 into the places of other radicals.

Methyl fluoride, CH_3F, is a gas obtained by heating potassium fluoride with potassium sulphomethylate, KCH_3SO_4. It is combustible, and produces hydrofluoric acid.

Ethyl fluoride has not been examined.

415. The dihydric alcohols or glycols, which contain two hydroxyl groups, yield haloid compounds in which either one or both of these are replaced by the halogen; thus, glycol, $C_2H_4(OH)_2$, yields glycol chlorhydrin, $C_2H_4.OH.Cl$, and $C_2H_4Cl_2$, already mentioned as *ethene dichloride*.

Glycol chlorhydrin, or *ethene hydrate chloride*, $C_2H_4(OH)Cl$, is prepared, though with difficulty, by the action of hydrochloric acid on glycol—

$$C_2H_4(OH)_2 + HCl = C_2H_4(OH)Cl + HOH.$$

It is a rather sweet liquid, of sp. gr. 1.24, and boiling point 128° C.; it mixes easily with water. Nascent hydrogen converts it into ethyl-alcohol—

$$C_2H_4(OH)Cl + H_2 = C_2H_5OH + HCl.$$

The corresponding bromine compound is obtained by the action of hydrobromic acid on ethene oxide; $C_2H_4O + HBr = C_2H_4(OH)Br$.

Ethene dichloride, or *Dutch liquid*, $C_2H_4Cl_2$, may be obtained from glycol by distilling it with phosphoric chloride—

$$C_2H_4(OH)_2 + 2PCl_5 = C_2H_4Cl_2 + 2POCl_3 + 2HCl;$$

but it is generally prepared by allowing equal volumes of dry ethene gas and dry chlorine to pass into a large inverted globe or flask, the neck of which passes through a cork into a receiver for the condensed liquid. It can also be obtained in quantity by passing olefiant gas, or even coal gas, into a warm mixture of

2 parts MnO_2, 3 parts NaCl, 4 parts water, and 5 parts H_2SO_4, till the black MnO_2 has disappeared, when ethene dichloride may be distilled off, accompanied, if coal gas be used, by propene dichloride in small quantity.

Ethene dichloride smells rather like chloroform; its sp. gr. is 1.28, and it boils at 83°.5 C.; it is nearly insoluble in water, but dissolves in alcohol.

Ethene dibromide, $C_2H_4Br_2$, is prepared by filling a Winchester quart bottle with olefiant gas, introducing 150 grammes of bromine and an equal volume of water, inserting a cork with a tube passing nearly to the bottom, and passing in olefiant gas, with frequent agitation, till the bromine is nearly decolorised. The product is shaken with a little weak soda solution, the lower layer separated, dried with calcium chloride, and distilled. It resembles the dichloride, but its sp. gr. is 2.16, and it boils at 129° C.

Ethene di-iodide, $C_2H_4I_2$, obtained by heating iodine in olefiant gas, forms silky needles, which may be sublimed in the gas, but are easily decomposed into C_2H_4 and I.

The difference in the stability of ethene chloride, bromide, and iodide is shown by the action of alcoholic solution of potash, which converts ethene dichloride into *monochlorethene*, or *vinyl chloride*; $C_2H_4Cl_2 + KHO = C_2H_3Cl + KCl + H_2O$; whilst the dibromide yields, in addition to the vinyl bromide, a quantity of acetylene; $C_2H_4Br_2 + 2KHO = C_2H_2 + 2KBr + H_2O$; and the di-iodide is much more easily decomposed, giving very little vinyl iodide and much acetylene.

Methene di-iodide, CH_2I_2, may be obtained by heating iodoform with strong hydriodic acid, in a sealed tube, to about 130° C., for some hours; $CHI_3 + HI = CH_2I_2 + I_2$. It is a liquid remarkable for its high specific gravity, 3.345, and is used for determining the specific gravities of precious stones. It boils at 182° C.

416. The trihydric alcohols, or glycerins, which contain three hydroxyl groups, yield haloid compounds in which one, two, or three of these are replaced by the halogen; thus, glycerin, $C_3H_5(OH)_3$, yields a *monochlorhydrin*, $C_3H_5(OH)_2Cl$, a *dichlorhydrin*, $C_3H_5.OH.Cl_2$, and a *trichlorhydrin*, $C_3H_5Cl_3$.

Monochlorhydrin and dichlorhydrin are prepared by saturating glycerin with hydrochloric acid, and heating for several hours to 100° C.; it is then neutralised with Na_2CO_3, and shaken with ether. On distilling the ethereal solution, the chlorhydrin comes over at about 227° C., which is its boiling point, whilst the dichlorhydrin boils at 174°, and is collected first. They are liquids, heavier than water, in which monochlorhydrin is more soluble than dichlorhydrin. They are both soluble in alcohol and ether. Potash converts dichlorhydrin into *epichlorhydrin*, $C_3H_5.O.Cl$, by removing HCl.

Trichlorhydrin, or *glyceryl trichloride*, or *allyl trichloride*, is obtained by the action of phosphoric chloride upon dichlorhydrin—

$$C_3H_5.OH.Cl_2 + PCl_5 = POCl_3 + HCl + C_3H_5Cl_3.$$

It is a liquid of pleasant smell, sp. gr. 1.42, and boiling at 158° C. It is sparingly soluble in water.

Bromine yields bromhydrins resembling those formed by chlorine, but the *tribromhydrin*, $C_3H_5Br_3$, is a crystalline solid. The iodine compound corresponding to this does not appear capable of existing.

Haloid allyl compounds.—Allyl chloride, C_3H_5Cl, is obtained by distilling allyl alcohol with phosphorus trichloride; $C_3H_5OH + PCl_3 = C_3H_5Cl + HCl + POCl$. It has a pungent smell, sp. gr. 0.95, and boiling point 46° C.; it is insoluble in water.

Allyl bromide may be prepared by distilling allyl alcohol with potassium bromide and sulphuric acid mixed with an equal bulk of water. It is capable of combining with bromine to form *glyceryl tribromide*, $C_3H_5Br_3$, and with hydrobromic acid to form $C_3H_6Br_2$, *trimethene dibromide*.

Allyl iodide, C_3H_5I, is prepared from glycerin (200 parts) by adding iodine (135), filling the retort with CO_2, and adding, very gradually, vitreous phosphorus (40). The distilled liquid is washed with a little NaHO, and dried with $CaCl_2$. Probably glyceryl tri-iodide is first produced; $C_3H_5(OH)_3 + P + I_3 = C_3H_5I_3 + P(OH)_3$; the tri-iodide is then decomposed into C_3H_5I and I_2. Allyl iodide has a very pungent odour of leeks, sp. gr. 1.85, and boiling point 101° C. It is remarkable for combining with mercury, shaken with its alcoholic solution, to form *mercury allyl iodide*, $Hg''C_3H_5I$, deposited in colourless crystals, which become yellow in light, and yield HgI_2 and C_3H_5I when treated with iodine. Ag_2O, in presence of H_2O, replaces the I by HO, producing $HgC_3H_5.HO$, *mercury allyl hydroxide*, an alkaline base. Bromine converts allyl iodide into tribromhydrin, $C_3H_5Br_3$.

417. *Haloid propargyl compounds.—Propargyl chloride*, C_3H_3Cl, is obtained by acting on propargyl alcohol with phosphorus chloride—

$$C_3H_3.OH + PCl_3 = C_3H_3Cl + POCl + HCl.$$

The bromide is obtained in a similar way; both these are liquids, but the iodide is a crystalline solid.

Haloid benzyl compounds.—Benzyl chloride, C_7H_7Cl, may be obtained from benzyl alcohol, $C_7H_7.OH$, by distilling with phosphoric chloride, but it is usually prepared by passing chlorine into toluene kept boiling in a retort with inverted condenser; $C_7H_8 + Cl_2 = C_7H_7Cl + HCl$. It boils at 176° C., giving tear-exciting vapours. The bromide resembles it, but boils at 201°. The iodide crystallises, but is unstable.

Cinnamyl, or *styryl chloride, bromide*, and *iodide* are formed when HCl, HBr, and HI act on the corresponding alcohol, $C_9H_9.OH$.

Cholesteryl chloride, $C_{26}H_{43}.Cl$, is obtained by the action of strong HCl on cholesterine; it crystallises from alcohol in needles.

Erythrite (p. 499), $C_4H_6(OH)_4$, when long heated with HCl, yields *erythrite dichlorhydrin*, $C_4H_6(OH)_2Cl_2$, a crystallisable solid. By employing phosphoric chloride, the *erythrite tetrachlorhydrin*, $C_4H_6Cl_4$, has been obtained.

Mannite (p. 499), $C_6H_8(OH)_6$, heated with strong HCl, yields *mannite dichlorhydrin*, $C_6H_8(OH)_4Cl_2$, a crystalline body soluble in water, but not in alcohol or ether. The corresponding bromide is insoluble. Dulcite gives similar compounds.

418. HALOID COMPOUNDS FORMED FROM THE ACIDS BY THE SUBSTITUTION OF A HALOGEN RADICAL FOR HYDROXYL.—These bodies, like those of the preceding class, have their counterparts among inorganic compounds; thus, if, in nitric acid, $NO_2.OH$, the OH be replaced by Cl, we obtain nitroxyl chloride, NO_2Cl; and, in acetic acid, $CH_3.CO.OH$, a similar exchange gives acetyl chloride, $CH_3.CO.Cl$.

No compound of this kind has been obtained from formic acid, and, since its formula would be $HCO.Cl$, it is intelligible that it should break up into HCl and CO, which have been the results of all efforts to obtain it.

419. *Acetyl chloride*, $CH_3.CO.Cl$, or *acetic oxychloride*, is prepared by distilling acetic acid with phosphorus trichloride; $3CH_3COOH + 2PCl_3 = 3CH_3COCl + P_2O_3 + 3HCl$. Three parts by weight of glacial acetic acid are gradually added to 2 parts of phosphorus trichloride, kept cool, and the mixture distilled on a water-bath. The distillate may be rectified over fused sodium acetate to remove any phosphorus trichloride.

Acetyl chloride is a colourless liquid, which fumes in air, and has an irritating odour; its sp. gr. is 1.11, and it boils at 55° C. Water decomposes it with violence, yielding hydrochloric and acetic acids; $CH_3.CO.Cl + HOH = CH_3.CO.OH + HCl$. If alcohol be employed instead of water, ethyl acetate is produced; $CH_3.CO.Cl + C_2H_5.OH = CH_3.CO.OC_2H_5 + HCl$. This mode of reaction renders acetyl chloride a most useful reagent for discovering the constitution of alcohols.

Some other instructive reactions produce acetyl chloride, such as that between acetic anhydride (di-acetyl oxide) and phosphoric chloride; $(C_2H_3O)_2O + PCl_5 = 2C_2H_3OCl + PCl_3O$; or between phosphorus oxychloride and sodium acetate—

$$PCl_3O + 2CH_3COONa = 2CH_3COCl + NaPO_3 + NaCl;$$

it was thus that acetyl chloride was first made. By distilling sodium acetate with acetyl chloride, acetic anhydride is obtained—

$$C_2H_3O.ONa + C_2H_3O.Cl = (C_2H_3O)_2O + NaCl.$$

By careful treatment with sodium-amalgam and snow, ethyl alcohol has been prepared from acetyl chloride—

$$C_2H_3OCl + H_4 = C_2H_5OH + HCl.$$

Acetyl bromide, $CH_3.CO.Br$, is prepared by distilling acetic acid with bromine and phosphorus; it resembles the chloride, but boils at 81° C., and becomes yellow when kept.

Acetyl iodide, $CH_3.CO.I$, is less stable, and is prepared by distilling acetic anhydride with iodine.

The haloid compounds formed from the higher members of the acetic series of acids are prepared in a similar manner, and generally resemble those of acetyl, but have higher boiling points.

Benzoyl chloride, or *benzoic chloride*, $C_6H_5.CO.Cl$, is prepared by distilling benzoic acid with phosphoric chloride; $C_6H_5.CO.OH + PCl_5 = POCl_3 + C_6H_5.CO.Cl$. It is a pungent smelling liquid, of sp. gr. 1.11, and boiling point 199° C. It is decomposed by water, but more slowly than acetyl chloride, yielding benzoic and hydrochloric acids. It may also be obtained by the action of chlorine on bitter-almond oil (benzoic aldehyd); $C_6H_5.CO.H + Cl_2 = C_6H_5.CO.Cl + HCl$. The benzoic bromide and iodide may be obtained by heating the chloride with KBr or KI.

Cinnamic chloride, $C_8H_7.CO.Cl$, obtained like the preceding, is an oily liquid boiling at 260° C.

Lactyl chloride, $C_2H_4.Cl.CO.Cl$, is formed when lactic acid is heated with phosphoric chloride; $C_2H_4.HO.CO.OH + 2PCl_5 = C_2H_4.Cl.CO.Cl + 2POCl_3 + 2HCl$. It is easily decomposed by water, yielding hydrochloric and *chloropropionic* acids; $C_2H_4Cl.CO.Cl + HOH = C_2H_4Cl.CO.OH + HCl$.

Salicylic chloride, $C_6H_4Cl.CO.Cl$, produced in a similar way from salicylic acid, yields *chlorobenzoic* acid when decomposed by water; $C_6H_4Cl.COCl + HOH = C_6H_4Cl.CO.OH + HCl$.

Succinyl dichloride, $C_2H_4(COCl)_2$, is obtained by distilling succinic acid with phosphoric chloride; $C_2H_4(CO.OH)_2 + 2PCl_5 = C_2H_4(COCl)_2 + 2POCl_3 + 2HCl$. It is a fuming liquid, of sp. gr. 1.39, boiling at 190° C. With water, it yields hydrochloric and succinic acids.

Fumaryl dichloride, $C_2H_2(CO.Cl)_2$, is the product of the distillation of fumaric acid, $C_2H_2(CO.OH)_2$, and of its isomeride, malæic acid, with phosphoric chloride. It boils at 160° C. Malic acid also yields fumaryl dichloride when distilled with phosphoric chloride; $C_2H_3.OH(CO.OH)_2 + 3PCl_5 = C_2H_2(CO.Cl)_2 + 3POCl_3 + 4HCl$.

Tartaric acid, $C_2H_2(OH)_2(CO.OH)_2$, heated with phosphoric chloride, is converted into *chloromalæic chloride*, $C_2HCl(CO.Cl)_2$, an oily liquid which yields crystals of *chloromalæic acid*, $C_2HCl(CO.OH)_2$, when decomposed by water.

Phthalyl dichloride, $C_6H_4(CO.Cl)_2$, is obtained by distilling phthalic acid, $C_6H_4(CO.OH)_2$, with phosphoric chloride. It is a yellow oily liquid, boiling at about 270° C. It is more stable than most other compounds of this class, being slowly decomposed by water into hydrochloric and phthalic acids. Even solution of NaHO only slowly decomposes it.

420. ETHEREAL SALTS FORMED FROM ACIDS BY THE SUBSTITUTION OF AN ALCOHOL RADICAL FOR BASYLOUS HYDROGEN.—These compounds (sometimes termed *esters*) are numerous and important, and correspond in composition to the salts formed by the substitution of metals for hydrogen in the acids. They may be formed from inorganic as well as from organic acids.

The ethereal salts exhibit a resemblance to the metallic salts in being decomposed by the hydroxides of the alkali-metals, with formation of the alcohol corresponding to the radical of the ethereal salt, and of a salt of the alkali-metal; thus, ethyl acetate, heated with potash, yields ethyl alcohol and potassium acetate—

$$CH_3.CO_2C_2H_5 + KHO = C_2H_5.HO + CH_3.CO_2K.$$

A reaction of this kind is termed the *saponification* of the ethereal salt, because the formation of soap is effected in a similar way by the action of alkalies on the fats and oils, which are ethereal salts formed by glycerin with the higher members of the acetic series of acids.

421. *Ethereal salts derived from sulphuric acid.—Hydromethyl sulphate*, or *sulphomethylic acid*, HCH_3SO_4, is prepared by slowly adding methyl alcohol (1 weight) to strong sulphuric acid (2 weights); the mixture, which becomes hot, is heated to boiling, cooled, and neutralised with barium carbonate, which precipitates the excess of sulphuric acid as barium sulphate, leaving *barium sulpho-*

methylate in solution; this is evaporated on a steam-bath, and finally *in vacuo*, when the barium salt crystallises in square tables having the composition $Ba(CH_3SO_4)_2.2Aq$. By dissolving this in water, and precipitating the barium with the correct quantity of sulphuric acid, a solution of sulphomethylic acid is obtained, which may be concentrated *in vacuo* to a syrupy acid liquid. The reaction between the methyl alcohol and sulphuric acid is

$$CH_3.OH + H_2SO_4 = CH_3HSO_4 + HOH,$$

but it can never be complete, on account of the accumulation of the water. Sulphomethylic acid is an unstable compound. At 130° C. it is decomposed into sulphuric acid and dimethyl sulphate, $2CH_3HSO_4 = (CH_3)_2SO_4 + H_2SO_4$. Boiled with water, it gives sulphuric acid and methyl alcohol; $CH_3HSO_4 + HOH = CH_3OH + H_2SO_4$. Heated with methyl alcohol, it gives methyl ether—

$$CH_3HSO_4 + CH_3.OH = CH_3.O.CH_3 + H_2SO_4.$$

Heated with alcohol, it gives methyl-ethyl ether—

$$CH_3HSO_4 + C_2H_5.OH = CH_3.O.C_2H_5 + H_2SO_4.$$

The basylous hydrogen in $HMeSO_4$ may be replaced by an equivalent weight of a metal, forming *sulphomethylates*, which are all soluble in water.

Sulphomethylic acid is formed when methyl alcohol is gradually added to well-cooled chlorosulphonic acid; $CH_3.OH + ClHO.SO_2 = HCl + HCH_3SO_4$. This shows the true relation in which sulphomethylic acid stands to sulphuric acid, $HO.HO.SO_2$; chlorosulphonic acid, $HO.Cl.SO_2$; sulphomethylic acid, $HO.CH_3O.SO_2$.

Dimethyl sulphate, $(CH_3)_2SO_4$, is prepared by gradually adding methyl alcohol (1 weight) to strong sulphuric acid (8 weights) and distilling the mixture. The portion which distils at 150° C. is shaken with water, and the lower layer rectified over $CaCl_2$. Much of the CH_3 group is, however, broken up in this process. A better result is obtained by distilling sulphomethylic acid at 130° under diminished pressure. The dimethyl sulphate is a liquid of peculiar odour, sp. gr. 1.32, and boiling point 188° C. It does not dissolve in water, but is slowly decomposed, yielding methyl alcohol and sulphomethylic acid. Many of its reactions resemble those of inorganic salts; thus, if distilled with NaCl, it yields methyl chloride, CH_3Cl, and Na_2SO_4. With sodium formate it gives methyl formate and Na_2SO_4.

Sulphethylic or *ethyl-sulphuric* or *sulphovinic acid*, $HC_2H_5SO_4$, is prepared in the same way as sulphomethylic acid, employing equal weights of alcohol and sulphuric acid. It is a viscid liquid, very similar in its properties and reactions to sulphomethylic acid. The sulphethylates are soluble and easily crystallisable salts. The *potassium sulphethylate*, $KC_2H_5SO_4$, obtained by decomposing the calcium salt with K_2CO_3, is much employed for the preparation of other ethyl salts by double decomposition. *Calcium sulphethylate*, $Ca(C_2H_5SO_4)_2.2Aq$, is obtained by gradually adding strong rectified spirit to twice its weight of strong sulphuric acid, heating to the boiling point, cooling, diluting with water, and neutralising with chalk. The calcium sulphate produced by the unconverted sulphuric acid is strained off, and the liquid evaporated on a steam-bath till it crystallises on cooling. The barium and lead sulphethylates also crystallise with 2Aq. *Silver sulphethylate*, $Ag.C_2H_5SO_4.Aq$, is soluble in water and alcohol.

Sulphethylic acid is formed when olefiant gas is absorbed by sulphuric acid; $C_2H_4 + H_2SO_4 = HC_2H_5SO_4$.

Di-ethyl sulphate, $(C_2H_5)_2SO_4$, is obtained by the reaction between ethyl iodide and silver sulphate in a sealed tube at 150° C.—

$$2C_2H_5I + Ag_2SO_4 = 2AgI + (C_2H_5)_2SO_4.$$

It is a fragrant liquid, of sp. gr. 1.18, and boiling point 208° C. It does not mix with water, and is scarcely decomposed by it in the cold; on heating, it yields alcohol and sulphethylic acid. Heated alone, it is decomposed into ethene and sulphuric acid; $(C_2H_5)_2SO_4 = 2C_2H_4 + H_2SO_4$.

Di-ethyl sulphate may also be obtained by passing vapour of SO_3 into well-cooled ether; $SO_3 + (C_2H_5)_2O = (C_2H_5)_2SO_4$. It is obtained as a secondary product in the preparation of ether, forming the bulk of the liquid called *heavy oil of wine*.

Sulphamylic or *amylsulphuric acid*, $HC_5H_{11}SO_4$, is formed by the action of strong sulphuric acid upon amyl alcohol; it is similar in properties to sulphethylic acid.

422. *Ethyl nitrate*, or *nitric ether*, $C_2H_5.NO_3$, is prepared by acting upon alcohol with nitric acid carefully purified from nitrous acid. It is not advisable to prepare it on a large scale, from the danger of explosion. 80 grms. of nitric acid of sp. gr. 1.4 are heated on a steam-bath, and about 2 grms. of urea nitrate are added to decompose any nitrous acid. After a time, the mixture is well cooled, and

15 grms. more urea nitrate are added, followed by 60 grms. of alcohol of sp. gr. 0.81. The mixture is carefully distilled on a steam-bath, the product being collected in fractions, of which the first is chiefly weak alcohol. The nitric ether is separated from the alcohol in the distillate by addition of water, shaken with addition of a very little potash, the lower layer separated, allowed to stand over fused calcium chloride, and distilled. The reaction between the alcohol and the nitric acid is $C_2H_5.OH + HNO_3 = C_2H_5.NO_3 + HOH$. The decomposition of the nitrous acid by the urea is expressed by $2HNO_2 + CO(NH_2)_2 = CO_2 + N_4 + 3H_2O$. When alcohol is mixed with ordinary nitric acid containing nitrous acid, the latter oxidises the alcohol to aldehyd and other products, which act upon the nitric acid in a very violent and sometimes explosive manner; but when urea is present, the nitrous acid acts on this instead of on the alcohol, and ethyl nitrate is tranquilly produced.

Ethyl nitrate has a very pleasant smell, and sp. gr. 1.1: it boils at 86° C., and its vapour explodes when heated, from the sudden disengagement of H_2O and CO_2. Water dissolves it very sparingly. Alcoholic solution of potash converts it into KNO_3 and alcohol.

Ethyl nitrite, $C_2H_5NO_2$, is the chief product of the action of nitric acid upon alcohol, until it becomes very violent, the nitric radical NO_3 being reduced to the nitrous radical NO_2 by the conversion of part of the alcohol into aldehyd. To prepare pure ethyl nitrite, 100 c.c. of solution containing 46 grms. of potassium nitrite are mixed with 50 c.c. of alcohol, and the solution is allowed to run slowly into a cooled mixture of 50 c.c. of alcohol, 100 c.c. of water, and 75 grms. of sulphuric acid. The ethyl nitrite is distilled over by the heat of reaction, and is condensed by ice. It is purified by shaking with a little dry potassium carbonate.

Ethyl nitrite is much lighter and more volatile than the nitrate, its sp. gr. being 0.9, and its boiling point 17° C. It has a yellowish colour, and a pleasant odour of apples. Like many other nitrous and nitric ethereal salts, it may be preserved unchanged if perfectly pure, but if water or other impurities be present, it decomposes, becoming acid, evolving red vapours, and bursting the bottle. Alcoholic potash converts it into KNO_2 and alcohol.

Ethyl nitrite is sometimes prepared by passing, into a mixture of 2 parts 85 per cent. alcohol and 1 part of water, kept very cool, the N_2O_3 obtained by heating 1 part of starch with 10 parts of nitric acid of sp. gr. 1.32. Much heat is evolved, and the receiver must be cooled in ice. The reaction is $2C_2H_5OH + N_2O_3 = H_2O + 2C_2H_5NO_2$. The N_2O_3 may be generated in contact with the alcohol by a due proportion of nitric acid and metallic copper; this is done in preparing the *spiritus ætheris nitrosi*, or *sweet spirit of nitre*, used in medicine; this is made by carefully adding 2 measured ounces of sulphuric acid to a pint of rectified spirit, slowly adding 2½ measured ounces of nitric acid to the cooled mixture, pouring it upon 2 ounces of fine copper wire in a retort with a good condenser, and distilling between 77° C. and 80°, until 12 measured ounces have distilled. Half an ounce more nitric acid is then poured into the retort, and three more ounces distilled over; the distillate is then mixed with two pints of rectified spirit. Hence the sweet spirit of nitre consists chiefly of spirit of wine, holding in solution ethyl nitrite, aldehyd, and some other products of the reaction. The proportion of ethyl nitrite present varies greatly, according to the efficiency of the condenser. Less is found in old samples, in consequence of volatilisation and chemical change. The presence of aldehyd is shown by the brown colour (aldehyd-resin) which it gives when shaken with alcoholic potash. Neglecting secondary changes, the formation of the ethyl nitrite in the above process may be represented by $C_2H_5.OH + HNO_3 + H_2SO_4 + Cu = C_2H_5NO_2 + CuSO_4 + 2H_2O$.

Methyl nitrite, CH_3NO_2, is a gas condensable by ice and salt. It may be produced from methyl alcohol by methods similar to those used for ethyl nitrite. It is produced when strong nitric acid acts upon the alkaloid brucine.

Methyl nitrate, CH_3NO_3, is a dangerously explosive body prepared like ethyl nitrate. Its sp. gr. is 1.18, and it boils at 66° C. It detonates under the hammer. It was formerly used in making aniline dyes, but it caused several accidents.

423. *Nitro-ethane* and *nitro-methane* are bodies having the same composition as ethyl and methyl nitrites, but with properties which show them to be *nitro-paraffins* or products of the substitution of NO_2 for H in paraffin hydrocarbons. Thus nitro-ethane, $C_2(NO_2)H_5$, results from the substitution of NO_2 for H in ethane, C_2H_6, and nitro-methane, $C(NO_2)H_3$, is derived in a similar way from

methane, CH_4. They are formed when ethyl iodide and methyl iodide are acted on by silver nitrite.

424. *Amyl nitrite*, $C_5H_{11}NO_2$, may be prepared by distilling amyl alcohol with potassium nitrite and sulphuric acid, or by passing N_2O_3 into amyl alcohol; it is a yellow liquid of sp. gr. 0.9, and boiling point 99° C. It has a remarkable smell, and the peculiar effect of its vapour when inhaled has led to its employment in medicine. The vapour of amyl nitrite explodes when heated.

The ethereal salts formed by phosphoric acid have no practical interest. When phosphoric anhydride is acted on by alcohol vapour, it deliquesces and yields a mixture of *phospho-monethylic acid*, $H_2C_2H_5PO_4$, *phospho-diethylic acid*, $H(C_2H_5)_2PO_4$, and *tri-ethylic phosphate*, $(C_2H_5)_3PO_4$.

Ethyl arsenite, $(C_2H_5)_3AsO_3$, is obtained by the reaction between sodium ethylate and arsenious chloride: $3C_2H_5ONa + AsCl_3 = (C_2H_5)_3AsO_3 + 3NaCl$. It has sp. gr. 1.22, and boils at 166° C. Water decomposes it according to the equation—

$$2(C_2H_5)_3AsO_3 + 3H_2O = 6C_2H_5OH + As_2O_3.$$

Ethyl borate, $(C_2H_5)_3BO_3$, or *boric ether*, is produced by the action of B_2O_3 on alcohol under pressure. It has the sp. gr. 0.8, and boils at 120° C. Its vapour burns with a green flame. It is decomposed by water into alcohol and boric acid.

Ethyl silicate, or *silicic ether*, $(C_2H_5)_4SiO_4$, is obtained by decomposing silicic chloride with alcohol; $SiCl_4 + 4C_2H_5OH = (C_2H_5)_4SiO_4 + 4HCl$. It has the sp. gr. 0.93, and boils at 165° C. Its vapour burns with a bright flame, evolving clouds of SiO_2. Moist air slowly decomposes it into alcohol and a hard mass of silicic acid. If the alcohol used in preparing it contains any water, *di-ethyl silicate*, $(C_2H_5)_2SiO_3$, is formed, which boils at 350° C.; $SiCl_4 + 2C_2H_5OH + H_2O = (C_2H_5)_2SiO_3 + 4HCl$. As might be expected from the chemical tendencies of silicon, several complex silicates and chlorosilicates of ethyl have been obtained.

One of the ethyl salts of carbonic acid is formed upon the imaginary type H_4CO_4, or *orthocarbonic acid*, so called because it may be represented as $C(HO)_4$ where the quadrivalent C is united to four univalent HO groups.

425. *Ethyl orthocarbonate*, $(C_2H_5)_4CO_4$, results from the action of sodium on an alcoholic solution of chloropicrin—

$$CCl_3NO_2 + 4C_2H_5OH + Na_4 = (C_2H_5)_4CO_4 + 3NaCl + NaNO_2 + H_4.$$

It boils at 158° C.

Ethyl carbonate, or *carbonic ether*, $(C_2H_5)_2CO_3$, is obtained by heating silver carbonate with ethyl iodide in a sealed tube. It boils at 126° C. Acted on by chlorine, it yields *perchlorethyl carbonate*, $(C_2Cl_5)_2CO_3$, a crystalline solid.

Potassium carbethylate, or *carborinate*, $KC_2H_5CO_3$, is produced when CO_2 is passed into a solution of HKO in absolute alcohol kept cool. The liquid and suspended precipitate are mixed with an equal volume of ether, and the precipitate treated with absolute alcohol, which dissolves the carbethylate, and yields it as a crystalline precipitate on adding ether. Water decomposes it into alcohol and hydro-potassium carbonate.

Ethyl perchlorate, $C_2H_5ClO_4$, is prepared by distilling barium perchlorate with barium sulphethylate; $Ba(ClO_4)_2 + Ba(C_2H_5SO_4)_2 = 2BaSO_4 + 2C_2H_5ClO_4$. It is a very explosive liquid, detonating even when slightly shaken; but if covered with a thin layer of water, it is more stable, and boils at 74° C.

The ethyl compounds have been chiefly taken as representatives of the ethereal salts of inorganic acids, but it must be understood that similar bodies may be formed with other alcohol-radicals.

426. The organic acids give rise to a large number of ethereal salts.

Methyl formate, HCO_2CH_3, is obtained by distilling sodium formate with potassium sulphomethylate; $HCO_2Na + KCH_3SO_4 = HCO_2CH_3 + KNaSO_4$. It is isomeric with acetic acid, CH_3CO_2H, but it boils at 36°. The whole of its hydrogen may be replaced by chlorine, yielding $ClCO_2CCl_3$, *chloromethyl formate*, which is decomposed by heat into $2COCl_2$, carbonyl chloride. Methyl formate is also produced when methyl alcohol is heated for some time with formic acid—

$$CH_3OH + HCO_2H = HCO_2CH_3 + HOH.$$

Methyl acetate, $CH_3CO_2CH_3$, is prepared by distilling methyl alcohol with dried lead acetate and sulphuric acid; it is a fragrant liquid, lighter than water, and boiling at 56° C. Unlike most ethereal salts, it mixes freely with water. It is a constituent of crude wood-spirit. Alkalies decompose it easily. It is metameric with propionic acid, $C_2H_5.CO_2H$.

Methyl oxalate, $(CO_2)_2(CH_3)_2$, is obtained by distilling methyl alcohol with an equal weight of sulphuric and oxalic acids; it solidifies in crystalline scales in the receiver; these fuse at 51° C., and boil at 162°. When distilled with water, methyl oxalate yields methyl alcohol and oxalic acid.

427. *Ethyl formate*, or *formic ether*, $HCO_2C_2H_5$, is prepared by distilling sodium formate (7 weights) with sulphuric acid (10) and alcohol (6). The distillate is freed from acid by shaking with a little lime, and redistilled. Formic ether is a fragrant liquid used for flavouring rum; it has sp. gr. 0.94, and boils at 55°. It dissolves in nine times its weight of water; the solution decomposes, when kept, into formic acid and alcohol. Formic ether is also prepared by heating molecular proportions of alcohol and oxalic acid with glycerin for some time in a retort with a reversed condenser, and distilling the product (see p. 509).

Ethyl formate is metameric with propylic acid.

Ethyl acetate, or *acetic ether*, $CH_3.CO_2C_2H_5$, is prepared by distilling alcohol with sodium acetate and sulphuric acid. 60 grammes of absolute alcohol are gradually added to 150 grms. of strong sulphuric acid; the cooled mixture is poured upon 100 grms. of fused sodium acetate, in small fragments, in a retort with a good condenser. The distillate is shaken with small quantities of saturated solution of salt, to remove alcohol, and the acetic ether, which rises to the surface, is drawn off, placed in contact with calcium chloride, to remove water, and distilled. Its production is expressed by the reaction—

$$C_2H_5.OH + H_2SO_4 + CH_3.CO_2Na = CH_3.CO_2.C_2H_5 + NaHSO_4 + HOH.$$

It may also be prepared by allowing a mixture of alcohol and acetic acid to flow into sulphuric acid heated to 130° C. (see p. 547).

Ethyl acetate is a fragrant liquid, smelling like cider; it has sp. gr. 0.91, and boils at 72° C. It requires about eleven times its weight of water to dissolve it, and the solution slowly decomposes into acetic acid and alcohol—

$$C_2H_5.C_2H_3O_2 + H_2O = HC_2H_3O_2 + C_2H_5.OH.$$

It mixes readily with alcohol and ether, and is useful as a solvent and for flavouring. In chemical research it is a valuable reagent, especially for the synthesis of acids. Chlorine converts it into *perchloracetic ether*, $CCl_3.CO_2.C_2Cl_5$, which smells like chloral. Iodine and aluminium acting together upon acetic ether give ethyl iodide and aluminium acetate—

$$6C_2H_5C_2H_3O_2 + Al_2 + 3I_2 = 6C_2H_5I + Al_2(C_2H_3O_2)_6.$$

Caustic alkalies, especially in alcoholic solution, easily *saponify* it, yielding acetates and alcohol; $C_2H_5.C_2H_3O_2 + KOH = C_2H_5.OH + KC_2H_3O_2$.

Ethyl acetate is metameric with butyric acid, which is remarkable for its unpleasant odour.

Ethyl aceto-acetate, or *acet-acetic ether*, $CH_2(C_2H_3O).CO_2C_2H_5$, is acetic ether in which one atom of H in the methyl group, CH_3, has been replaced by acetyl, (C_2H_3O), and is prepared by acting upon acetic ether with sodium, treating the product with acetic acid, diluting with water, and distilling the light oil which separates; the ether distils over at about 180° C. The first action of sodium upon acetic ether appears to produce sodium-ethylate and *sodium-triacetyl*—

$$3(C_2H_3O.OC_2H_5) + Na_4 = 3(C_2H_5.ONa) + Na(C_2H_3O)_3.$$

The sodium ethylate then reacts, with more acetic ether, to form alcohol and *sodacetic ether*; $C_2H_5.ONa + C_2H_3O.OC_2H_5 = C_2H_5.OH + C_2(H_2Na)O.OC_2H_5$. This last, acting upon another molecule of acetic ether, exchanges hydrogen for acetyl, and becomes *sodio-acet-acetic ether*—

$$C_2H_3O.OC_2H_5 + C_2(H_2Na)O.OC_2H_5 = C_2H(C_2H_3O)NaO.OC_2H_5 + HO.C_2H_5.$$

When sodio-acet-acetic ether is decomposed by acetic acid, it yields sodium acetate and acet-acetic ether—

$$C_2H(C_2H_3O)NaO.OC_2H_5 + HC_2H_3O_2 = NaC_2H_3O_2 + C_2H(C_2H_3O)HO.OC_2H_5.$$

Acet-acetic ether smells of hay. It is partly decomposed by distillation, unless in a current of steam. When treated with acids, alkalies, or with water under pressure, it yields acetone, alcohol, and CO_2; $C_2H(C_2H_3O)HO.OC_2H_5 + H_2O = CH_3.CO.CH_3 + C_2H_5.OH + CO_2$. It gives a violet colour with ferric chloride.

When heated with ethyl iodide, sodio-acet-acetic ether exchanges its sodium for ethyl, producing ethyl acet-acetic ether, $C_2H(C_2H_3O)(C_2H_5)O.OC_2H_5$, which gives a blue colour with ferric chloride.

By reactions similar to the above, we may obtain di-ethyl acet-acetic ether; $C_2(C_2H_3O)(C_2H_5)_2O.OC_2H_5$.

By decomposing acet-acetic ether with potash, potassium acet-acetate is obtained, and from this there is obtained *acet-acetic acid*, $CH_2(C_2H_3O)CO_2H$.

Acet-acetic ether will be seen hereafter to be a very important reagent for the synthesis of acids and ketones.

When vapour of ethyl aceto-acetate is passed through a red-hot tube, it yields *dehydracetic acid*, $C_7H_7O_2.CO_2H$, which forms sparingly soluble fusible crystals. It is unchanged by the strongest acids, but is decomposed by alkalies according to the equation $C_8H_8O_4 + 3H_2O = CO_2 + CH_3.CO.CH_3$ (*acetone*) $+ 2(CH_3.CO_2H)$. Dehydracetic acid is metameric with vanillic acid, $C_6H_3.OH.OCH_3.CO_2H$.*

428. *Ethyl butyrate*, or *butyric ether*, $C_3H_7.CO_2C_2H_5$, prepared by distilling butyric acid with alcohol and sulphuric acid, is sold as *ananas oil*, or *essence of pineapple*, which it resembles in odour. It is usually sold dissolved in alcohol, from which water precipitates it. The mixture of butyric acid and its homologues, obtained by decomposing butter with superheated steam, is used for preparing it.

Ethyl pelargonate, or *pelargonic ether*, $C_8H_{17}.CO_2C_2H_5$, prepared from essential oil of rue (p. 503), is used in flavouring under the name of *quince oil*, and appears to be present in the fruit.

Ethyl caprate, or *capric ether*, $C_9H_{19}.CO_2C_2H_5$, was formerly called *œnanthic ether*, because it is found in old wine. It is made by distilling wine-lees, and, when pure, is a colourless, fragrant, oily liquid of sp. gr. 0.87, boiling at 187° C. It is sold for flavouring.

Amyl acetate, $CH_3.CO_2C_5H_{11}$, is sold as *pear-essence;* and is prepared by distilling fousel oil (p. 492) with acetic and sulphuric acids; it boils at 133° C.

Amyl valerate, $C_4H_9.CO_2C_5H_{11}$, or *apple oil*, is obtained by distilling fousel oil with sodium valerate and sulphuric acid; its boiling point is 188° C.

Amyl caprate, $C_9H_{19}.CO_2C_5H_{11}$, is found in Hungarian wine.

The ethyl salts of acids of the acetic series containing more than ten atoms of carbon are generally prepared by dissolving the acids in alcohol, and passing hydrochloric acid gas into the solution; probably this converts the alcohol into ethyl chloride, which acts upon the acid to form the ethyl salt; this is deposited in crystals from the alcoholic solution. Ethyl palmitate and stearate are very fusible crystalline solids.

429. *Cetyl palmitate*, $C_{15}H_{31}.CO_2.C_{16}H_{33}$, constitutes the chief part of the crystalline fat, *spermaceti*, occurring in the skull of the sperm whale; it fuses at 49° C. It is saponified by alkalies with some difficulty, and yields *cetylic alcohol*, or *ethal*, $C_{16}H_{33}.OH$, and an alkaline palmitate.

Ceryl cerotate, $C_{26}H_{53}.CO_2.C_{27}H_{55}$, composes *Chinese wax*, the produce of an insect of the cochineal tribe.

Melissyl palmitate, or *myricin*, $C_{15}H_{31}.CO_2.C_{30}H_{61}$, forms about one-third of *bees'-wax*, the colour, odour, and tenacity of which appear to be due to the presence of a greasy substance called *cerolein*, which composes about 5 per cent. of the wax.

Melissyl melissate, $C_{29}H_{59}.CO_2.C_{30}H_{61}$, is contained in hay, and may be extracted by boiling alcohol.

430. *Ethyl benzoate*, or *benzoic ether*, $C_6H_5.CO_2.C_2H_5$, is prepared by dissolving benzoic acid in alcohol, saturating with hydrochloric acid gas, distilling, and mixing the distillate with water, when ethyl benzoate separates as a fragrant liquid, of sp. gr. 1.05, boiling at 211° C. A test for alcohol is afforded by the production of the odour of benzoic ether on heating with benzoyl chloride—

$$C_7H_5O.Cl \ + \ C_2H_5.OH \ = \ C_7H_5O_2C_2H_5 \ + \ HCl.$$

Benzyl benzoate, $C_6H_5.CO_2.C_7H_7$, is a fusible crystalline substance contained in *balsam of Peru*.

Benzyl cinnamate, $C_8H_7.CO_2.C_7H_7$, is present in the balsams of Peru and Tolu; it was formerly called cinnaméin.

Methyl salicylate, $C_6H_4.OH.CO_2.CH_3$, occurs in *oil of winter-green*, extracted from the flowers of *Gaultheria procumbens*, and was one of the first vegetable products prepared artificially. It is obtained by distilling methyl alcohol with sulphuric acid and salicylic acid. It is a fragrant liquid of sp. gr. 1.2, and boiling point 224° C. Ferric chloride colours it violet. On treating it with strong solution of soda, in the cold, it yields crystals of $C_6H_4.ONa.CO_2.CH_3$. When this is heated with methyl iodide in a sealed tube, it gives $C_6H_4.OCH_3.CO_2.CH_3$, or *methylic methylsalicylate*, an oily liquid. If this be saponified by potash, it yields the potassium salt of *methyl-salicylic acid*, $C_6H_4.OCH_3.CO_2H$, a crystalline acid isomeric with methyl salicylate, but not giving the violet colour with ferric chloride. The *ethyl salicylate* resembles the methyl compound.

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* Its constitution has been investigated by W. H. Perkin, jun. (*Chem. Soc. Journ.* June 1887).

431. *Ethyl oxalate*, or *oxalic ether*, $(CO_2.C_2H_5)_2$, is prepared by distilling alcohol with oxalic acid. Equal weights of dried oxalic acid and absolute alcohol are boiled for six hours in a retort with a reversed condenser. The product is mixed with water, which separates the oxalic ether as a fragrant liquid of sp. gr. 1.09, boiling at 186° C. It is decomposed, by boiling with water, into alcohol and oxalic acid. Potash easily decomposes it, and if it be mixed with only half the quantity of potash required for complete decomposition, it yields pearly scales of potassium oxalethylate; $(CO_2.C_2H_5)_2 + KHO = (CO_2)_2KC_2H_5 + C_2H_5.HO$. By decomposing this with hydrofluosilicic acid, *oxalethylic* or *oxalovinic acid*, $(CO_2)_2C_2H_5.H$, is obtained, but it is easily decomposed by water.

By the action of sodium on an ethereal solution of ethyl oxalate and ethyl acetate, the sodium derivative of *ethyl oxalacetate* is obtained; this has the formula $CO_2C_2H_5.CO.CH_2.CO_2C_2H_5$, and, when heated with dilute sulphuric acid, yields *pyruvic acid*, $CH_3.CO.CO_2H$, which is convertible into lactic acid by nascent hydrogen.

Ethyl malonate, or *malonic ether*, $CH_2(CO_2.C_2H_5)_2$, is prepared by passing HCl gas into absolute alcohol containing calcium malonate in suspension –

$$CH_2(CO_2)_2Ca + 2(C_2H_5.HO) + 2HCl = CH_2(CO_2.C_2H_5)_2 + CaCl_2 + 2HOH.$$

After some hours' standing, the liquid is boiled on a steam-bath, again saturated with HCl gas, the alcohol distilled off, the liquid neutralised with sodium carbonate, and mixed with water, when the malonic ether separates as a bitter aromatic liquid of sp. gr. 1.068, and boiling point 195° C. It resembles acetic ether in allowing its hydrogen to be displaced by sodium, and is a useful reagent for the synthesis of the fatty acids.

Cinnamyl cinnamate, or *styracin*, $C_8H_7.CO_2.C_9H_9$, is a crystalline ethereal salt obtained from *storax* by treatment with soda.

Ethyl malate, or *malic ether*, $C_2H_3.OH(CO_2.C_2H_5)_2$, obtained by the action of HCl gas on an alcoholic solution of malic acid, is a liquid which mixes with water, but is easily decomposed by it, yielding alcohol and malic acid.

Ethyl tartrate, or *tartaric ether*, $C_2H_2.(OH)_2.(CO_2C_2H_5)_2$, is prepared like malic ether, the acid liquid being neutralised with soda and shaken with ether, which extracts the ethyl tartrate; it cannot be distilled without decomposition. Water decomposes it easily, producing alcohol, and *acid ethyl tartrate*, or *tartrethylic acid*, $C_2H_2(OH)_2.CO_2.C_2H_5.CO_2H$.

Ethyl citrate, or *citric ether*, $C_3H_4.OH(CO_2.C_2H_5)_3$, is prepared in the same way as the tartrate; it is liquid and sparingly soluble in water; distillation decomposes it.

Methyl picrate, $C_6H_2(NO_2)_3O.CH_3$, is produced by decomposing silver picrate with methyl iodide, or by acting with nitric acid upon anisol, *phenyl-methyl ether*, $C_6H_5.O.CH_3$. It forms yellow crystals, which may be sublimed.

Ethyl picrate, or *picric ether*, $C_6H_2(NO_2)_3O.C_2H_5$, formed by the action of ethyl iodide on silver picrate, also crystallises.

The ethereal salts of an alcohol radical may be converted into those of another alcohol radical by mixing them with the alcohol in question, and adding a small quantity of a metallic alcoholate, the action of which has not been fully explained. Thus, methyl oxalate dissolved in ethyl alcohol, and mixed, in the cold, with a small quantity of sodium alcohol, $C_2H_5.ONa$, becomes in great measure converted into ethyl oxalate, and, conversely, ethyl oxalate is transformed into methyl oxalate by dissolving it in methyl alcohol, and adding a minute quantity of sodium methylate.

432. *Ethereal salts derived from glycol.*—These are very numerous, because either one or both of the OH groups in $C_2H_4(OH)_2$ may be replaced, and two different radicals may be introduced. None of them, however, as yet possess any practical importance.

Ethene-sulphuric acid, $H_2C_2H_4(SO_4)_2$, is formed when glycol acts upon chlorosulphonic acid; $C_2H_4(OH)_2 + 2(SO_2.OH.Cl) = H_2C_2H_4(SO_4)_2 + 2HCl$. It is a liquid which is decomposed when heated with water, giving glycol and sulphuric acid, just as its analogue, sulphethylic acid, gives alcohol and sulphuric acid.

Ethene hydroxysulphuric acid, $C_2H_4.OH.SO_4H$, formed when glycol is heated with H_2SO_4, is known only in its salts.

Ethene nitrate, $C_2H_4(NO_3)_2$, is an oily explosive liquid resembling nitroglycerin, and obtained by the action of a mixture of nitric and sulphuric acids upon glycol.

Ethene nitrite, $C_2H_4(NO_2)_2$, is a crystalline solid which may be fused and sublimed with only partial decomposition.

Ethene di-acetate, $(CH_3.CO_2)_2C_2H_4$, is obtained by acting on ethene dibromide with silver acetate, or by heating glycol with acetic acid to 200° C. It is a heavy liquid, with an acetic smell, boiling at 186° C. It is fairly soluble in water.

Ethene monacetate, $CH_3.CO_2.OH.C_2H_4$, is also formed from glycol and acetic acid, and resembles the di-acetate.

Ethene acetobutyrate has the formula $CH_3.CO_2.OC_4H_7O.C_2H_4$.

433. *Ethereal salts derived from glycerol.*—These compounds, often termed *glycerides*, are even more numerous than those derived from glycol, since the three OH groups in $C_3H_5(OH)_3$ may each be replaced by a different radical. The glycerides are of great practical interest, because they include most of the animal and vegetable fats. They are sometimes termed the salts of *propenyl* (C_3H_5).

Sulphoglyceric acid, $C_3H_5(OH)_2SO_4H$, is formed, with considerable evolution of heat, when glycerol is dissolved in strong sulphuric acid. The acid may be obtained as in the case of sulphethylic acid. It is only known in solution, being easily decomposed even by evaporation *in vacuo*. It is important as being produced in the process of *saponification by sulphuric acid*, in which the natural fats or glycerides are decomposed by that acid, leaving the fatty acid in the free state.

434. *Nitroglycerin*, or *glyceryl trinitrate*, $C_3H_5(NO_3)_3$, has been already noticed (p. 498). It is a heavy oily liquid, of sp. gr. 1.6, without smell, very explosive, and poisonous. It is insoluble in water, sparingly soluble in alcohol, but soluble in ether and in methyl alcohol. When saponified by potash it yields glycerol and potassium nitrate. Its formation is explained in the following equation—

$$\underset{\text{Glycerin.}}{C_3H_8O_3} + 3(HNO_3) = \underset{\text{Nitroglycerin.}}{C_3H_5(NO_3)_3} + 3H_2O.$$

On a large scale, a mixture of concentrated nitric acid (sp. gr. 1.47 to 1.49) with twice its weight of concentrated sulphuric acid is employed. The mixture is placed in stone jars containing about 7 lbs. each, which are immersed in running water, and about 1 lb. of glycerin (sp. gr. 1.25) is gradually added, with frequent stirring, to the contents of each jar, care being taken that the temperature does not rise above 80° F. The mixture is allowed to settle for a quarter of an hour, and poured gradually into 5 or 6 gallons of water. The oily nitroglycerin which falls to the bottom is well washed by stirring with water, a little alkali being added in the last washings. One per cent. of magnesia is sometimes added to the nitroglycerin in order to neutralise any acid arising from decomposition.

This oil is very violent in its explosive effects. If a drop of nitroglycerin be placed on an anvil and struck sharply, it explodes with a very loud report, even though not free from water; and if a piece of paper moistened with a drop of it be struck, it is blown into small fragments. On the application of a flame or of a red-hot iron to nitroglycerin, it burns quietly; and when heated over a lamp in the open air it explodes but feebly. In a closed vessel, however, it explodes at about 360° F. with great violence. For blasting rocks, the nitroglycerin is poured into a hole in the rock, *tamped* by filling the hole with water, and exploded by the concussion caused by a detonating fuze (see page 564). It has been stated to produce the same effect in blasting as ten times its weight of gunpowder, and much damage has occurred from the accidental explosion of nitroglycerin in course of transport. When nitroglycerin is kept, especially if it be not thoroughly washed, it decomposes, with evolution of nitrous fumes and formation of crystals of oxalic acid; and it may be readily imagined that, should the accumulation of gaseous products of decomposition burst one of the bottles in a case of nitroglycerin, the concussion would explode the whole quantity.

Nitroglycerin, like gun-cotton, is particularly well fitted for blasting, because it will explode with equal violence whether moisture be present or not, but it has the advantage of containing enough oxygen to convert all its carbon into carbonic acid gas. On the other hand, it is very poisonous, and is said to affect the system seriously by absorption through the skin, and the gases resulting from its explosion are exceedingly acrid. Again, its fluidity prevents its use in any but downward bore-holes. To overcome these objections, and to diminish the danger of transport, several blasting compounds have been proposed, of which nitroglycerin is the basis.

Dynamite is composed of a particularly porous siliceous earth (*Kieselguhr*), obtained from Oberlohe in Hanover, impregnated with about 70 or 75 per cent. of nitroglycerin.

Kieselguhr contains 63 per cent. of soluble silica, about 18 of organic matter, 11 of sand and clay, and 8 of water. It is incinerated to expel the organic matter, and mixed with the nitroglycerin in wooden troughs lined with lead. When used in solid rock, dynamite is six or seven times as strong as blasting-powder.

Nobel's detonators for nitroglycerin contain 7 parts of mercuric fulminate and 3 parts of potassium chlorate, pressed into small copper tubes.

Fatal accidents have occurred in using dynamite, in consequence of exudation of nitroglycerin from the dynamite, caused by contact with water in the bore-holes, this nitroglycerin having been afterwards exploded by the drill in boring fresh holes.

Glyoxylin is a name given to gun-cotton pulp and saltpetre mixed with nitroglycerin. *Lithofracteur* is a more complex mixture containing about half its weight of nitroglycerin, together with nitrate of soda, sulphur, powdered coal, sawdust, and siliceous earth. *Dualin* is composed of nitroglycerin and sawdust. *Nitromagnite* contains nitroglycerin and magnesia.

Blasting gelatin is made by dissolving collodion-cotton in about nine times its weight of nitroglycerin; its detonation is even more powerful than that of nitroglycerin itself. The readiness with which it may be exploded by a detonating fuze charged with mercuric fulminate is greatly increased by incorporating it with about one-tenth of its weight of gun-cotton. On the other hand, its liability to accidental detonation may be reduced by intimately mixing it with a small proportion of camphor, the action of which does not appear to be understood.

Nitroglycerin is readily soluble in ether and in wood-naphtha, but somewhat less so in alcohol; it is reprecipitated by water from these last solutions. It becomes solid at 40° F., a circumstance which is unfavourable to its use in mining operations, partly because it is then less susceptible of explosion by the detonating fuze, and partly because serious accidents have resulted from attempts to thaw the frozen nitroglycerine by heat, or to break it up with tools. It is remarkable that, when made on the small scale, the nitroglycerin may generally be cooled down to 0° F. without becoming hard. This and other observations render it probable that some other substitution product is occasionally mixed with it.

Nitroglycerin, $C_3H_5(NO_3)_3$, stands in the same relation to the tri-atomic alcohol glycerin, $C_3H_5(HO)_3$, in which nitric ether, $C_2H_5(NO_3)$, stands to ordinary mon-atomic alcohol, $C_2H_5(HO)$. Berthelot finds that, in the formation of nitric ether by the action of nitric acid upon alcohol, 5800 heat units are disengaged for each molecule of nitric acid entering into the reaction, whereas, in the formation of nitroglycerin, only 4300 heat units, per molecule of nitric acid, are disengaged. Less energy having been converted into heat in the latter case, more is stored up in the nitroglycerin, and hence its formidable effect as an explosive. In the formation of gun-cotton, each molecule of nitric acid disengaged 11,000 heat units, to which Berthelot attributes the stability and inferior explosive effect of gun-cotton in comparison with nitroglycerin.

435. *Glyceryl mononitrate*, $C_3H_5(OH)_2NO_3$, is produced by the action of dilute nitric acid on glycerol; it is also liquid, but soluble in water, and not explosive.

Glyceryl-phosphoric or *phosphoglyceric acid*, $C_3H_5(OH)_2PO_4H_2$, is formed by the action of metaphosphoric acid on glycerol, but has only been obtained in solution. It is a product of decomposition of *lecithin*, a fatty substance containing phosphorus, which occurs in the brain and other parts of the body, and in fish and the yolk of eggs.

Glyceryl arsenite, $C_3H_5.AsO_3$, is obtained by dissolving white arsenic in glycerol, and evaporating; $2C_3H_5(OH)_3 + As_2O_3 = 2C_3H_5AsO_3 + 3HOH$. It forms a yellowish glass, fusing at 50° C. It is sometimes used for fixing aniline dyes.

Glyceryl borate, or *boroglyceride*, $C_3H_5BO_3$, is prepared from boric acid and glycerol; it is also a transparent glass, dissolving slowly in water, and has been recommended for the preservation of food.

436. Glycerol forms numerous ethereal salts with the fatty acids.

Monoformin, $C_3H_5(OH)_2.CO_2H$, and *diformin*, $C_3H_5.OH.(CO_2H)_2$, are produced when oxalic acid is heated with glycerol in making formic acid—

$$C_3H_5(OH)_3 + (CO_2H)_2 = C_3H_5(OH)_2.CO_2H + CO_2 + H_2O.$$

Tri-acetin, $C_3H_5(C_2H_3O_2)_3$, is present in cod-liver oil, and may be obtained by acting on glycerol with acetic acid.

Tributyrin, $C_3H_5(C_4H_7O_2)_3$, occurs in butter.

Tripalmitin, or *palmitin*, $C_3H_5(C_{16}H_{31}O_2)_3$, is obtained from palm-oil or from Chinese wax, by pressing and crystallising from alcohol. It fuses at 46° C.

Tristearin, or *stearin*, $C_3H_5(C_{18}H_{35}O_2)_3$, is prepared by repeatedly recrystallising the harder natural fats, such as tallow, from their solution in ether. It fuses at 63° C.

Tri-olein, or *olein*. $C_3H_5(C_{18}H_{33}O_2)_3$, is obtained by cooling olive-oil to 0° C., pressing out the liquid part, dissolving this in a little alcohol, again freezing, to separate the rest of the stearin, and distilling off the alcohol. Olein is less easily decomposed by alkalies than palmitin and stearin, and is left unaltered when olive-oil is treated with a cold concentrated solution of NaHO, which converts the palmitin and stearin into soaps and glycerol.

The three glycerides, palmitin, stearin, and olein, are found in most animal and vegetable fats. *Olive-oil* and *Chinese wax* consist almost entirely of palmitin and olein. Palm-oil contains all three. *Mutton suet* is chiefly stearin, with a little palmitin and olein. *Beef suet* contains more palmitin; these constitute *tallow*. *Lard* has a similar composition. *Human fat* contains more palmitin. *Goose fat* and *butter* contain, beside the above glycerides, those of volatile acids, such as butyric, capric, caprylic, and caproic. *Cocoa-nut oil* contains *trilaurin*, $C_3H_5(C_{12}H_{23}O_2)_3$.

Palmitin, *stearin*, and *olein* may be made artificially by heating glycerol with the corresponding acids; for example—

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid.}}{3HC_{18}H_{35}O_2} = \underset{\text{Stearin.}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3HOH.$$

437. ORGANO-MINERAL COMPOUNDS, *formed upon the type of the chlorides of mineral elements by the substitution of organic radicals for the chlorine.*—The preparation of most of the compounds of this class requires the aid of *zinc di-ethide*, $Zn(C_2H_5)_2$, which will therefore be described first. It is obtained by the action of metallic zinc upon ethyl iodide—

$$Zn_2 + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2.$$

Eight hundred grains (or 50 grms.) of bright, freshly granulated, and thoroughly dried zinc are placed in a half-pint flask (E, fig. 281), which is connected with the carbonic acid apparatus (A), from which the gas is passed through strong sulphuric acid in the bottles (B and C), where it is thoroughly dried. A second perforation in the cork of the flask (E) allows the passage of the tube *f*, which passes through the two corks in the wide tube F, and dips into a little mercury in D. A stream of cold water is kept running through the wide tube (F), being conveyed by the caoutchouc tubes *t t*. When the whole apparatus has been filled with carbonic

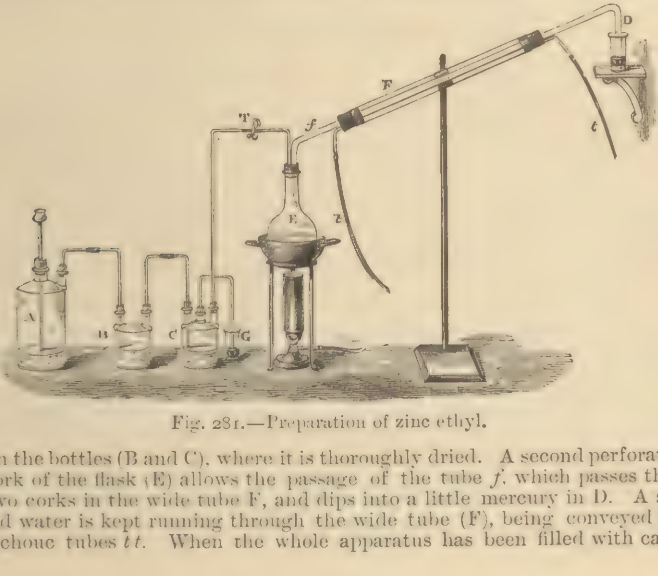

Fig. 281.—Preparation of zinc ethyl.

acid gas, the cork of the flask (E) is removed, and 400 grains (or 25 grms.) of ethyl iodide (perfectly free from moisture) are introduced, the cork being then replaced.* The carbonic acid gas is again passed for a short time, and then cut off by closing the nipper-tap (T) upon a caoutchouc connector, when the gas escapes through the tube (G), which dips into mercury. A gentle heat is then applied by a water bath to the flask (E) till the ethyl iodide boils briskly, the vapour being condensed in the tube *f*, and running back into the flask. In about five hours the conversion is complete, and the iodide ceases to distil. The nipper-tap (T) is again opened, and a slow current of carbonic acid gas is allowed to pass; the position of the condenser (F) is reversed (fig. 282), and the tube *f* is connected, by the cork K, with the short test-tube O; the longer limb of a very narrow siphon (I) of stout tube passes through a second perforation in the cork (K), the shorter limb passing into the very short test-tube (P), the cork of which is also furnished with the short piece of moderately wide tube (L). For receiving and preserving the zinc ethyl, a number of small tubes are prepared of the form shown in fig. 283. The long narrow neck (R) of one of these is passed down the short tube (L) to the bottom of P, the other end (N) of the tube being connected with an apparatus for passing dry carbonic acid gas. The whole of the apparatus being filled with this gas, the nipper-tap is closed, and the flask (E) heated on a sand-bath, so that the zinc ethyl may distil over, a slow stream of carbonic acid gas being constantly passed into P, the excess escaping through L. When enough zinc ethyl has collected in the tube (O), a blowpipe flame is applied to the narrow tube (N), which is drawn off and sealed; the siphon tube (I) is then gradually pushed down, so that its longer limb may be sufficiently immersed in the zinc ethyl, and the nipper-tap (T, fig. 281) is opened, when the pressure of the carbonic acid gas forces over a part of the zinc ethyl into the tube P. By heating the tube (M) with a spirit-lamp, so as to expel part of the gas, allowing it to cool, it will become partly filled with zinc ethyl, and may be withdrawn and quickly sealed by the blow-pipe. The spontaneous inflammability of the zinc ethyl, and its easy decomposition by water, render great care necessary in its preparation. If an alloy of zinc with one-fourth its weight of sodium be employed, the conversion may be effected in an hour.

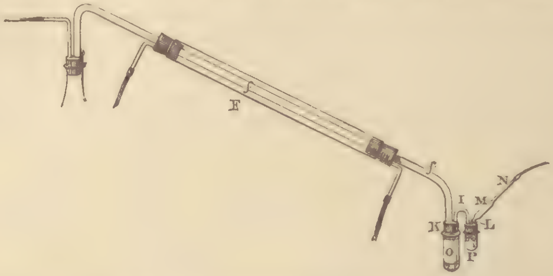

Fig. 282.—Collection of zinc ethyl.

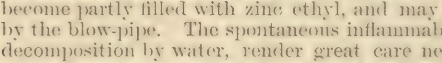

Fig. 283.

The reaction in the preparation of zinc di-ethide really takes place in two stages; when the ethyl iodide ceases to distil, the flask contains *zinc iodo-ethide*, $ZnIC_2H_5$, as a crystalline solid, which is decomposed by a higher temperature into zinc ethide and zinc iodide; $2ZnIC_2H_5 = Zn(C_2H_5)_2 + ZnI_2$. The action takes place more quickly if the zinc be polarised by copper in the copper-zinc couple. To effect this, cupric oxide is reduced by heating it in a tube in a current of hydrogen or coal-gas, and 10 grammes of it are mixed with 90 grammes of zinc-filings in a 300 cubic centimetre flask, which is then heated over a Bunsen burner, with continual shaking, until it forms grey granular masses. After cooling, 87 grammes of ethyl iodide are added, heated to about 90° C. with the reversed condenser, till no more liquid distils back, which requires about 15 minutes; the rest of the operation is conducted as described above, using a sand-bath or an oil-bath.

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* The process is said to be much accelerated if about $\frac{1}{50}$th of zinc ethyl is dissolved in the ethyl iodide.

Properties of zinc di-ethide.—It is a colourless liquid of peculiar odour, sp. gr. 1.18, and boiling point 118° C. In contact with air it inflames spontaneously, burning with a bright greenish blue flame, emitting a white smoke of ZnO. If a piece of porcelain be depressed upon the flame, a deposit of metallic zinc is formed, surrounded by a ring of oxide, yellow while hot and white on cooling. When zinc ethide is dissolved in ether and acted on by oxygen, it yields *zinc di-ethylate*, $Zn(OC_2H_5)_2$, corresponding to zinc hydrate, $Zn(OH)_2$, as a white powder. Water decomposes it readily, with evolution of ethane or ethyl hydride in the state of gas; $Zn(C_2H_5)_2 + H_2O = ZnO + 2(C_2H_5.H)$. When ammonia is passed into the solution of zinc ethide in ether, ethyl hydride is evolved, and a white precipitate of zinc amide is deposited—

$$Zn(C_2H_5)_2 + 2NH_3 = 2(C_2H_5.H) + Zn(NH_2)_2.$$

Zinc ethide and ethyl iodide, dissolved in ether and heated to 170° C., yield butane, or di-ethyl; $Zn(C_2H_5)_2 + 2C_2H_5I = ZnI_2 + 2(C_2H_5)_2$. Heated with sulphur, zinc ethide is converted into *zinc mercaptide*, $Zn(SC_2H_5)_2$, the analogue of zinc ethylate and zinc hydrate. Zinc ethide is much used in organic research, especially for effecting the substitution of C_2H_5 for Cl, Br, I, or HO.

438. *Zinc dimethide*, or *zinc methyl*, $Zn(CH_3)_2$, is prepared from methyl iodide by a process similar to that for zinc ethide, which it resembles, but is far more volatile, boiling at 46° C., and has a more powerful odour, producing irritation. It is more energetic in its reactions than zinc ethide, and is decomposed, with inflammation and explosion, by water, yielding methyl hydride gas, or methane; $Zn(CH_3)_2 + H_2O = ZnO + 2(CH_3.H)$. When acted on by methyl iodide, it yields ethyl hydride; $Zn(CH_3)_2 + 2CH_3I = 2CH_2(CH_3) + ZnI_2$. By slow oxidation, zinc methide yields a crystalline compound, *zinc methyl methylate*, $ZnCH_3.OCH_3$, smelling of camphor. When this is treated with water, it gives methyl alcohol, methane, and zinc hydrate; $ZnCH_3.OCH_3 + 2HOH = Zn.OH.OH + CH_3.H + CH_3.OH$.

Methyl alcohol acts upon zinc methide in two stages, producing, first, zinc methyl methylate and methane; $CH_3.OH + Zn(CH_3)_2 = Zn.CH_3.OCH_3 + CH_3.H$; and, in the second stage, zinc methylate and methane—

$$Zn.CH_3.OCH_3 + CH_3.OH = Zn(OCH_3)_2 + CH_3.H.$$

Zinc methide combines with the ethers; it forms with methyl ether the compound $2Zn(CH_3)_2.(CH_3)_2O$, which boils at the same temperature as zinc methide.

When zinc methide is dissolved in ether, and heated with sodium in a sealed tube, one-third of the zinc is displaced by sodium, forming a crystalline compound of zinc methide with sodium methide—

$$3Zn(CH_3)_2 + Na_2 = 2(Zn(CH_3)_2.NaCH_3) + Zn.$$

If this be exposed, in a tube, to a current of dry carbon dioxide, zinc methide distils off, and sodium acetate remains in the tube; $NaCH_3 + CO_2 = CH_3.CO_2Na$. By treating the compound of zinc ethide with sodium ethide in the same way, sodium propylate is obtained; $NaC_2H_5 + CO_2 = C_2H_5.CO_2Na$.

Boron trimethide, $B(CH_3)_3$, is formed by the action of a strong ethereal solution of zinc methide upon ethyl borate—

$$2(C_2H_5)_3BO_3 + 3Zn(CH_3)_2 = 2B(CH_3)_3 + 3Zn(O.C_2H_5)_2.$$

It is a gas with an intolerably pungent, tear-exciting odour, liquefied by three atmospheres pressure. When issuing very slowly into the air, it undergoes partial oxidation, with phosphorescence, but when it comes rapidly into contact with air, it burns with a green flame, remarkable for the immense quantity of large flakes of carbon which it emits. It combines with ammonia, forming $NH_3.B(CH_3)_3$, which crystallises from an ethereal solution, and may be sublimed. −3°C

Silicon tetramethide, $Si(CH_3)_4$, produced by the action of $SiCl_4$ upon zinc methyl, is a liquid lighter than water, burning in air, and producing a white smoke of silica. It is not decomposed by water, and boils at 30° C. *Silicon tetrethide*, or *silicium ethide*, $Si(C_2H_5)_4$, obtained by a similar process, resembles the methyl compound, but boils at 153° C. In its chemical relations it resembles the paraffin hydrocarbons, and is sometimes called *silico-nonane*, the ninth member of the paraffin series, C_9H_{20}, in which silicon replaces an atom of carbon. When acted on by chlorine, it yields $SiC_8H_{19}Cl$; when this is heated with potassium acetate, in alcoholic solution, it yields the acetate $SiC_8H_{19}.C_2H_3O_2$, and by heating this with alcoholic solution of potash, it is converted into *silico-nonyl alcohol*, $SiC_8H_{19}.OH$, boiling at 190°.

By acting upon ethyl orthosilicate, $Si(OC_2H_5)_4$, with zinc ethide and sodium, metallic zinc is separated, and the resulting sodium ethide effects the replacement of the *ethoxyl* group, OC_2H_5, by ethyl. In this way there are produced *silicon triethyl-ethylate*, $Si(C_2H_5)_3.OC_2H_5$, *silicon diethyl-diethylate*, $Si(C_2H_5)_2(OC_2H_5)_2$, and *silicon ethyl-triethylate*, $SiC_2H_5(OC_2H_5)_3$. When this is heated with acetyl chloride, it yields *silicon ethyl-trichloride*, $Si.C_2H_5.Cl_3$, which is converted by water into *silico-propionic acid*, $C_2H_5.SiO.OH$, according to the equation—

$$SiC_2H_5Cl_3 + 2H_2O = C_2H_5.SiO.OH + 3HCl.$$

It is a solid body, having weak acid properties. *Silico-acetic acid*, $CH_3.SiO.OH$, is a similar body derived from zinc methide and ethyl silicate.

439. *Boron tri-ethide*, or *triborethyl*, $B(C_2H_5)_3$, may be prepared like the corresponding methyl compound; or by passing vapour of boron trichloride into zinc di-ethide; $2BCl_3 + 3Zn(C_2H_5)_2 = 2B(C_2H_5)_3 + 3ZnCl_2$. It is a colourless liquid of irritating odour, and insoluble in water. Its sp. gr. is 0.69, and it boils at 95° C.

It inflames spontaneously in air, burning with a green flame, and explodes in contact with pure oxygen. Water slowly converts it into $B(C_2H_5)_2OH$, another spontaneously inflammable liquid.

By gradual oxidation in air, borethyl is converted into $B.C_2H_5.(OC_2H_5)_2$, in which two oxethyl groups, OC_2H_5, are substituted for two ethyl groups. This is a liquid which may be distilled *in vacuo*, and is decomposed by water, yielding alcohol and *ethyl-boric acid*, $B.C_2H_5(OH)_2$, which is a volatile crystalline body, subliming in scales like boric acid, and having a very sweet taste and a pleasant smell; it is very soluble in water, alcohol, and ether.

Trimethyl phosphine, $P(CH_3)_3$, is prepared by very gradually dropping PCl_3 into a solution of zinc methide in ether, in a retort connected with a receiver filled with CO_2; a very violent action takes place, according to the equation—

$$2PCl_3 + 3Zn(CH_3)_2 = 3ZnCl_2 + 2P(CH_3)_3.$$

The condensed liquid forms two layers, the upper containing the excess of PCl_3 and ether, the lower being a compound of zinc chloride with trimethyl phosphine, which may be separated by careful distillation with potash in a retort filled with H. Trimethyl phosphine is a spontaneously inflammable liquid with a most remarkable odour. It boils at about 40° C. When slowly oxidised, it yields a crystalline solid, $P(CH_3)_3O$, after the type PCl_3O. It also combines with S and with Cl_2.

Methyl iodide combines with trimethyl phosphine to form *tetramethylphosphonium iodide*, $P(CH_3)_4I$, a colourless crystalline body corresponding to phosphonium iodide, PH_4I (p. 233). By treating this with silver oxide and water, it is converted into the corresponding hydroxide, $P(CH_3)_4.OH$, a strongly alkaline body; $2P(CH_3)_4I + Ag_2O + H_2O = 2P(CH_3)_4OH + 2AgI$.

By heating phosphonium iodide with methyl iodide and zinc oxide, in a sealed tube, to 100° C. for some hours, the hydriodides of *methyl phosphine*, $P.CH_3.H_2$, and *dimethyl phosphine*, $P(CH_3)_2H$, are obtained—

$$2PH_4I + 2CH_3I + ZnO = ZnI_2 + H_2O + 2(P.CH_3.H_2.HI)\text{; and}$$
$$PH_4I + 2CH_3I + ZnO = ZnI_2 + H_2O + P(CH_3)_2H.HI.$$

These hydriodides are obtained in the form of crystalline compounds with the zinc iodide. By the action of water in a distilling apparatus filled with hydrogen, the methyl phosphine is evolved as gas, leaving the dimethyl phosphine to be liberated by the addition of potash.

Methyl phosphine is a very strong-smelling gas, easily liquefied by cold, and quickly oxidised by air. Though not alkaline, it combines with acids to form crystalline salts which bleach litmus-paper, a piece of which, wetted and dipped into an acid, when exposed to methyl-phosphine gas, will have only the red part bleached. The action of strong nitric acid converts it into *methyl-phosphinic acid*, $PCH_3O(OH)_2$. Dimethyl phosphine is a spontaneously inflammable liquid, which boils at 25° C. It combines with acids to form salts. Nitric acid converts it into *dimethyl-phosphinic acid*, $P(CH_3)_2O.OH$.

440. *Tri-ethyl phosphine*, $P(C_2H_5)_3$, may be prepared by the action of PCl_3

on zinc ethide, as for trimethyl phosphine, or by heating phosphonium iodide with alcohol, in a sealed tube, to 180° C.; $PH_4I + 3C_2H_5OH = P(C_2H_5)_3.HI + 3HOH$. The hydriodide thus obtained is distilled with potash. Tri-ethyl phosphine is a liquid having a strong odour, of sp. gr. 0.81, and boiling at 127° C. It absorbs O, and becomes hot when exposed to air, and its vapour explodes with O below 100°. It forms salts with the acids. Tri-ethyl phosphine, in its chemical characters, resembles the corresponding methyl compound. Its oxide, $P(C_2H_5)_3O$, is a very stable crystalline substance, which may be obtained by distilling *tetrethyl-phosphonium iodide* with potash, ethyl hydride being produced at the same time; $P(C_2H_5)_4I + KOH = P(C_2H_5)_3O + KI + C_2H_5.H$. The tetrethyl-phosphonium iodide may be obtained by heating ethyl iodide with phosphorus in a sealed tube; $4C_2H_5I + P_2 = P(C_2H_5)_4I + PI_3$. By decomposing the aqueous solution of $P(C_2H_5)_4I$ with silver oxide, the iodine is replaced by OH, producing *tetrethyl-phosphonium hydroxide*, $P(C_2H_5)_4OH$, a strongly alkaline substance, which may be crystallised. Tri-ethyl phosphine combines violently with methyl iodide, forming $P(C_2H_5)_3CH_3.I$, which yields an alkaline hydroxide when decomposed with water and silver oxide.

Tri-ethyl phosphine combines with sulphur, evolving heat, and forming $P(C_2H_5)_3S$, which crystallises in needles from solution in hot water. Tri-ethyl phosphine also combines energetically with carbon disulphide, forming a fine red crystalline compound soluble in alcohol. The presence of a trace of CS_2 in coal gas is at once indicated by the red colour with tri-ethyl phosphine. When the red compound is boiled with water, it yields the oxide and sulphide of tri-ethyl phosphine, carbon disulphide, and methyl tri-ethyl phosphonium hydroxide—

$$4P(C_2H_5)_3CS_2 + 2H_2O = P(C_2H_5)_3O + 2P(C_2H_5)_3S + 3CS_2 + P(C_2H_5)_3.CH_3.OH.$$

Ethyl phosphine, $P.C_2H_5.H_2$, and *di-ethyl phosphine*, $P(C_2H_5)_2H$, are prepared like the methyl compounds. Ethyl phosphine is liquid, boiling at 25° C. It has an intolerable odour, is insoluble in water, and possesses weak basic properties. Di-ethyl phosphine is also liquid, but boils at 85° C., and is more strongly basic. Both compounds, being composed upon the PCl_3 model, are disposed to unite with other bodies to form compounds upon the PCl_5 model. When oxidised by nitric acid, they yield, respectively, *ethyl-phosphinic*, $P.C_2H_5.O(OH)_2$, and *di-ethyl-phosphinic* acid, $P(C_2H_5)_2.O.OH$, composed upon the model of orthophosphoric acid, $PO(OH)_3$, by the substitution of ethyl for hydroxyle.

441. *Trimethyl arsine*, $As(CH_3)_3$, is obtained by the action of $AsCl_3$ on zinc methide. It is a strong-smelling liquid, boiling at about 70° C., and resembling trimethyl phosphine, but not forming salts with the acids.

Arsen-dimethyl, or *kakodyl*, $As(CH_3)_2$, has a special interest as one of the first bodies to be recognised as a compound radical capable of behaving like an elementary substance. The formula $As(CH_3)_2$ represents only one volume of vapour, so that it must be doubled to represent a molecule, conveniently termed *dikakodyl*, and the symbol Kd may be used to represent the uncombined radical or atomic group $As(CH_3)_2$.

The oldest compound of kakodyl is the *dikakodyl oxide*, Kd_2O, or *alcarsin*, or *arsenical alcohol*, named, after its discoverer, Cadet's fuming liquid, and obtained by distilling a mixture of equal weights of white arsenic and potassium acetate—

$$As_2O_3 + 4CH_3CO_2K = [As(CH_3)_2]_2O + 2CO_2 + 2K_2CO_3.$$

The distillate has a strong odour of garlic, and takes fire spontaneously, which is due to the presence of dikakodyl. It is received in water, when it sinks to the bottom. Its sp. gr. is 1.46, and it boils at 150° C. Dikakodyl oxide combines with acids to form salts. It dissolves in alcohol, and the solution gives, with mercuric chloride in alcoholic solution, a crystalline precipitate of $Kd_2O.2HgCl_2$. By distilling this with strong HCl in a retort filled with CO_2, *kakodyl chloride*, KdCl, is obtained as a heavy spontaneously inflammable liquid, of terrible odour. When this is heated to 100° C. in contact with zinc in an atmosphere of CO_2, a compound of zinc chloride with kakodyl is produced, and, on treating this water, dikakodyl separates as a heavy oily liquid which boils at 170° C. It inflames spontaneously in air, and, when its vapour is passed through a tube heated to 400° C., it is decomposed as in the equation $As_2(CH_3)_4 = 2CH_4 + C_2H_4 + As_2$. When slowly oxidised by air, it is converted into Kd_2O, which is afterwards converted, in presence of water, into *kakodylic acid*, KdO.OH, or *dimethyl-arsinic acid*, $As(CH_3)_2O.OH$, representing arsenic acid, $AsO(OH)_3$, in which two OH groups are replaced by $(CH_3)_2$. This acid is best prepared by oxidising Kd_2O with mercuric oxide in presence of water—

$$Kd_2O + 2HgO + H_2O = 2KdO_2H + Hg_2.$$

It crystallises from the aqueous solution, and is a stable acid. Sulphur dissolves in dikakodyl, forming Kd_2S, a colourless liquid of unpleasant smell, which behaves like an alkaline sulphide. Kd_2S_2 is a solid which may be crystallised from alcohol.

Kakodyl cyanide, KdCN, is prepared by distilling kakodyl chloride with mercuric cyanide; $2KdCl + Hg(CN)_2 = 2KdCN + HgCl_2$. It forms lustrous prismatic crystals, fusing at 37° C. and boiling at 140°. It is nearly insoluble in water, but dissolves in alcohol. Its vapour is extremely poisonous.

Kakodyl trichloride, $As(CH_3)_2Cl_3$, is composed upon the model of $AsCl_5$, whilst the chloride, $As(CH_3)_2Cl$, is formed after $AsCl_3$. The chloride ignites in chlorine, but, if it be dissolved in carbon disulphide, the action of Cl converts it into crystals of the trichloride. When this is heated, it evolves methyl chloride gas, and a heavy irritating liquid distils over, which is *arsenmethyl dichloride*, $AsCH_3Cl_2$, boiling at 133°, and soluble in water without decomposition. By evaporating the solution with sodium carbonate, and extracting the residue with alcohol, *arsenmethyl oxide*, $AsCH_3O$, may be crystallised from the alcoholic solution. The crystals smell like assafœtida. Mercuric oxide, in the presence of water, converts the oxide into *methyl-arsinic acid*, $AsCH_3O(OH)_2$.

When dikakodyl is acted on by methyl iodide, it yields kakodyl iodide and *tetramethyl-arsonium iodide*, as in the equation—

$$As_2(CH_3)_4 + 2CH_3I = As(CH_3)_2I + As(CH_3)_4I;$$

this last, when decomposed by moist silver oxide, yields the corresponding hydroxide, $As(CH_3)_4OH$, which is strongly alkaline, and may be crystallised.

Pentamethyl arsine, $As(CH_3)_5$, corresponding to $AsCl_5$, has been obtained.

442. *Tri-ethyl arsine*, $As(C_2H_5)_3$, is prepared like the methyl compound, which it resembles. It boils at about 140° C., and is rapidly oxidised by air, forming $As(C_2H_5)_3O$. It also combines directly with sulphur, bromine, and iodine, forming

$As(C_2H_5)_3S$, $As(C_2H_5)_3Br_2$, $As(C_2H_5)_3I_2$, composed upon the model of $AsCl_5$. Triethyl arsine is a weak base: its nitrate may be crystallised. When heated with ethyl iodide, it yields the compound $As(C_2H_5)_4I$, which, when decomposed by moist Ag_2O, yields *tetrethyl-arsonium hydroxide*, $As(C_2H_5)_4OH$, a crystallisable alkaline body behaving like KOH.

Di-ethyl arsine, or *ethyl kakodyl*, $As_2(C_2H_5)_4$, is formed by the action of sodium arsenide on ethyl iodide. It resembles dimethyl arsine, but is not spontaneously inflammable, though it oxidises very rapidly in air. It boils at about 190° C.

Antimony forms compounds with the alcohol radicals, composed upon the models $SbCl_3$ and $SbCl_5$.

Stibio trimethyl, or *trimethyl stibine*, $Sb(CH_3)_3$, is obtained by heating methyl iodide with the potassium antimonide which is obtained by strongly heating tartar-emetic (p. 353): $3CH_3I + K_3Sb = 3KI + (CH_3)_3Sb$. The powdered antimonide must be mixed with sand to moderate the action, and the distillation must take place in CO_2. The product is a garlic-smelling liquid, of sp. gr. 1.5, and boiling at 80° C. It is insoluble in water, but dissolves in ether. By the slow action of air it is converted into $Sb(CH_3)_3O$, but it is liable to take fire. It combines with chlorine and iodine, forming $Sb(CH_3)_3Cl_2$ and $Sb(CH_3)_3I_2$, which may be crystallised, and are formed upon the model of $SbCl_5$. The iodide is formed when powdered antimony is heated to 140° C., in a sealed tube, with methyl iodide; $9CH_3I + Sb_4 = 3Sb(CH_3)_3I_2 + SbI_3$. Stibio trimethyl combines at once with methyl iodide, forming $Sb(CH_3)_4I$ as a white solid, crystallising in six-sided plates from hot water. When decomposed by Ag_2O in presence of water, it yields a strong caustic alkali, *tetramethyl-stibonium hydroxide*, $Sb(CH_3)_4OH$, which may be crystallised, and forms crystallisable salts. The nitrate, $Sb(CH_3)_4NO_3$, forms crystals like nitre. Even the carbonates correspond to those of the alkalies; thus, the normal carbonate is $[Sb(CH_3)_4]_2CO_3$, and the acid carbonate $Sb(CH_3)_4.HCO_3$.

Stibio pentamethyl, $Sb(CH_3)_5$, composed on the model of $SbCl_5$, is obtained by distilling stibio-trimethyl iodide with zinc methide—

$$Sb(CH_3)_3I_2 + Zn(CH_3)_2 = Sb(CH_3)_5 + ZnI_2.$$

Stibio tri-ethyl, or *tri-ethyl stibine*, $Sb(C_2H_5)_3$, is obtained like stibio trimethyl; or by acting on antimonious chloride with zinc ethide: $2SbCl_3 + 3Zn(C_2H_5)_2 = 2Sb(C_2H_5)_3 + 3ZnCl_2$. It resembles the methyl compound, but boils at 158° C. It is remarkable for behaving like a metal; even decomposing hydrochloric acid and liberating hydrogen: $Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2$. The chloride is an oily liquid smelling like turpentine. The bromide and iodide are obtained by mixing a well-cooled alcoholic solution of stibio tri-ethyl with alcoholic solutions of bromine and iodine; the bromide is liquid, and is separated on adding water to the alcoholic solution: the iodide crystallises, and behaves like potassium iodide with reagents. The sulphide, $Sb(C_2H_5)_3S$, is obtained in colourless crystals by dissolving sulphur in an ethereal solution of stibio tri-ethyl. It behaves with acids and with metallic salts like an alkaline sulphide; thus, $CuSO_4 + Sb(C_2H_5)_3S = CuS + Sb(C_2H_5)_3SO_4$. This sulphate, as well as the nitrate, $Sb(C_2H_5)_3(NO_3)_2$, are evidently formed, not on the model of the ammonium salts, but on that of $SbCl_5$. The nitrate may be crystallised in large prisms from a solution of stibio tri-ethyl or its oxide in nitric acid. It explodes when heated.

If a solution of stibio tri-ethyl in ether be allowed to evaporate in the air, and the residue washed with alcohol and ether, a white residue is left, which is soluble in water, and has the composition $Sb(C_2H_5)_3(SbO_2)_2$.

When stibio tri-ethyl and ethyl iodide are mixed under water, they combine to form $Sb(C_2H_5)_4I$, which solidifies, and may be crystallised in prisms from hot water. From this, by the action of silver oxide, *tetrethyl-stibonium hydroxide*, $Sb(C_2H_5)_4.OH$, is obtained as a caustic alkaline liquid, yielding, with acids, salts corresponding in composition to the ammonium-salts.

The hydrosulphide, $Sb(C_2H_5)_4.SH$, gives reactions resembling those of KSH or NH_4SH.

443. *Bismuth tri-ethyl*, $Bi(C_2H_5)_3$, is prepared by acting on ethyl iodide with an alloy of potassium and bismuth. It is a spontaneously inflammable liquid which is very unstable, depositing bismuth even below 100° C., and exploding at 150°. As might be expected from the non-existence of $BiCl_5$, bismuth tri-ethyl shows no disposition to combine directly with the halogens, its derivatives being formed on the model of $BiCl_3$. Thus, when it is mixed, in alcoholic solution, with mercuric chloride; $Bi(C_2H_5)_3 + 2HgCl_2 = BiC_2H_5.Cl_2 + 2(Hg.C_2H_5.Cl)$; the mercuric ethyl chloride is precipitated, and the bismuth ethyl dichloride crystallises from the

solution. By reaction with KI, this yields $Bi.C_2H_5.I_2$, sparingly soluble in water, but crystallising from alcohol, the solution in which gives, with potash, a yellow precipitate of $Bi.C_2H_5.O$, which is spontaneously inflammable.

The compounds of lead with alcohol radicals are not composed upon the model of the stable chloride, $PbCl_2$, but upon that of $PbCl_4$, which is not known in the pure state.

Lead tetramethyl, $Pb(CH_3)_4$, is formed by the action of zinc-methyl upon lead chloride; $2Zn(CH_3)_2 + 2PbCl_2 = 2ZnCl_2 + Pb(CH_3)_4 + Pb$; it distils over at 110° C., and has the sp. gr. 2.03. It has a faint odour, is unaffected by air, and is insoluble in water. When heated with hydrochloric acid—

$$Pb(CH_3)_4 + HCl = Pb(CH_3)_3Cl + CH_4.$$

The chloride is crystalline, and may be sublimed; by reaction with potassium iodide, it gives colourless crystals of $Pb(CH_3)_3I$, and when this is distilled with potash, $Pb(CH_3)_3.OH$ is obtained as a strongly alkaline body smelling like oil of mustard.

Lead tetrethyl, $Pb(C_2H_5)_4$, and its derivatives resemble the methyl compounds. It boils at 200°, and deposits metallic lead, but may be distilled unchanged in a current of steam.

Lead tri-ethyl, $Pb(C_2H_5)_3$, is obtained by the action of ethyl iodide upon an alloy of sodium and lead. This combines with iodine in alcoholic solution, forming $Pb(C_2H_5)_3I$, from which, by means of Ag_2O, the hydroxide, $Pb(C_2H_5)_3.OH$, is obtained as a strongly alkaline crystalline body, the smell of which excites sneezing. It forms salts by exchanging the OH for an equivalent amount of acid radicals.

444. *Mercuric methide*, $Hg(CH_3)_2$, may be obtained by the reaction between mercuric chloride and zinc methide, but a better method of preparing it is to dissolve one part of sodium in one hundred parts of mercury, and to add the amalgam, by degrees, to methyl iodide mixed with one-tenth of its volume of acetic ether, the action of which has not yet been explained. On distillation, the mercuric methide is obtained as a colourless liquid which is one of the heaviest known, its sp. gr. being 3.07, so that glass floats in it. It is unchanged by exposure to air, but gives off a faint odour which is very poisonous. It boils at 95° C., and burns with a bright flame. When acted on by strong hydrochloric acid, $Hg(CH_3)_2 + HCl = HgCH_3Cl + CH_3.H$.

The *mercury methyl chloride* is crystalline, and sparingly soluble in water. The iodide, $HgCH_3I$, is formed by keeping methyl iodide in contact with mercury in sunshine, or by adding iodine to an alcoholic solution of mercuric methide; $Hg(CH_3)_2 + I_2 = HgCH_3I + CH_3I$. It is insoluble in water, but crystallises from alcohol, and may be sublimed. It yields an alkaline solution of the hydroxide, $Hg.CH_3.OH$, with Ag_2O.

The nitrate, $Hg.CH_3.NO_3$, is obtained crystallised by decomposing the iodide with silver nitrate; and the sulphate, $(HgCH_3)_2SO_4$, is formed when strong sulphuric acid acts on mercuric methide, methane being evolved as gas.

Mercuric ethide, $Hg(C_2H_5)_2$, is prepared like the methide, but with an amalgam containing only $\frac{1}{500}$th of sodium. It has the sp. gr. 2.4, and boils at 159° C. Its vapour is decomposed at 200° C. into mercury and butane, C_4H_{10}.

Mercury ethyl chloride, HgC_2H_5Cl, is obtained by acting on mercuric ethide with mercuric chloride dissolved in alcohol; $Hg(C_2H_5)_2 + HgCl_2 = 2HgC_2H_5Cl$: this shows it to be composed upon the mercuric type, $HgCl_2$, and not derived from the mercurous compound $Hg_2(C_2H_5)_2$, corresponding to Hg_2Cl_2. The chloride is insoluble in water, but crystallises from alcohol, and is easily sublimed. Silver oxide converts it into the *mercury ethyl hydroxide*, HgC_2H_5OH, a caustic alkaline liquid which blisters the skin. The iodide, HgC_2H_5I, obtained like the methyl compound, is remarkably stable, crystallising from hot caustic soda, almost without decomposition. It is hardly soluble in water or alcohol. Hydrocyanic acid, in alcoholic solution, converts the hydroxide into the cyanide, HgC_2H_5CN, which is crystalline, volatile, and of very poisonous odour.

The sulphide, $(HgC_2H_5)_2S$, forms a yellowish precipitate by ammonium sulphide in an alcoholic solution of the chloride. It may be crystallised from ether. The sulphate and nitrate of mercury ethyl resemble the methyl compounds.

445. *Tin tetramethide*, $Sn(CH_3)_4$, composed upon the model of stannic chloride, $SnCl_4$, is obtained by the action of an alloy of tin, mercury, and sodium upon methyl iodide. It boils at 78° C. By the action of iodine, one methyl group is removed, and *tin trimethyl iodide*, $Sn(CH_3)_3I$, is obtained, and this, acted on by NaOH, yields $Sn(CH_3)_3OH$, a sparingly soluble, crystalline, volatile, alkaline base.

When methyl iodide is heated to 160° C., in a sealed tube, with tin-foil, *tin dimethyl iodide*, $Sn(CH_3)_2I_2$, is formed. It crystallises in yellow prisms which dissolve in water, and give a white precipitate of $Sn(CH_3)_2O$, a basic substance, on adding ammonia.

Tin tetrethide, or *stannic ethide*, $Sn(C_2H_5)_4$, is prepared by distilling stannic chloride with zinc ethide. It has the sp. gr. 1.19, and boils at 181° C. It is remarkably stable, not being decomposed even when boiled with sodium. It is not precipitated by H_2S.

Stannous ethide, $Sn_2(C_2H_5)_4$, composed upon the model of two molecules of stannous chloride, $SnCl_2$, is prepared by the action of ethyl iodide upon an alloy of tin with one-fourth of its weight of sodium. After the reaction, ether extracts $Sn_2(C_2H_5)_4$ and $Sn_2(C_2H_5)_6$. The ethereal solution is evaporated in CO_2, and the mixture treated with alcohol, which leaves the hexethide undissolved. On adding water to the alcoholic solution, the stannous ethide separates as an oily liquid of sp. gr. 1.56, having a musty odour. When heated, it is decomposed; $Sn_2(C_2H_5)_4 = Sn(C_2H_5)_4 + Sn$. As would be expected, stannous ethide behaves as an unsaturated compound, absorbing oxygen from the air, and forming $Sn(C_2H_5)_2O$, which is insoluble in water, alcohol, and ether, but dissolves in nitric acid, forming $Sn(C_2H_5)_2(NO_3)_2$, and in sulphuric acid, forming $Sn(C_2H_5)_2SO_4$, both of which may be crystallised; they are evidently composed upon the $SnCl_4$ type.

Tin hexethide, $Sn_2(C_2H_5)_6$, is composed upon the model of the unknown chloride, Sn_2Cl_6, corresponding to the oxide, Sn_2O_3. Its preparation is described above. It is an oily liquid of powerful odour, boiling at 270°, but decomposing into $Sn(C_2H_5)_4$ and Sn. It combines with iodine, forming $2Sn(C_2H_5)_3I$. When this is distilled with KOH, it yields $Sn(C_2H_5)_3OH$, which passes over with the steam and crystallises in prisms. This hydroxide is a very strong alkaline base, which yields crystallisable salts; the nitrate is $Sn(C_2H_5)_3.NO_3$, and the sulphate $[Sn(C_2H_5)_3]_2SO_4$. If $Sn(C_2H_5)_3I$ be heated with sodium ethylate, $NaOC_2H_5$, the *tin tri-ethyl ethylate*, $Sn(C_2H_5)_3.OC_2H_5$, distils over. This is evidently composed upon the $SnCl_4$ model, three chlorine atoms being replaced by ethyl, and the fourth by ethoxyl, OC_2H_5, which represents hydroxyl, OH. Water decomposes it, yielding alcohol and $Sn(C_2H_5)_3.OH$.

The chloride, $Sn(C_2H_5)_3Cl$, formed when HCl acts on the hydroxide, is a liquid crystallising at 0° C. The iodide is also liquid, even below 0°.

When tin hexethide is heated with hydrochloric acid—

$$Sn_2(C_2H_5)_6 + 4HCl = 2Sn(C_2H_5)_2Cl_2 + 2C_2H_5H + H_2.$$

446. *Aluminium methide*, $Al_2(CH_3)_6$, and the corresponding *ethide* are obtained by decomposing mercuric methide and ethide by aluminium; $3Hg(CH_3)_2 + Al_2 = Hg_3 + Al_2(CH_3)_6$. They are spontaneously inflammable liquids, which are violently decomposed by water, yielding $Al_2(OH)_6$ and methane or ethane.

At high temperatures their vapour-densities lead to the molecular formulæ $Al(CH_3)_3$ and $Al(C_2H_5)_3$. By heating ethyl iodide with aluminium, $Al_2(C_2H_5)_3I_3$ is obtained.

Magnesium methide, $Mg(CH_3)_2$, and *ethide* are prepared by decomposing methyl or ethyl iodide with magnesium, when a solid iodide, $MgCH_3I$, is first formed, which is decomposed when distilled in CO_2; $2MgCH_3I = Mg(CH_3)_2 + MgI_2$. They are spontaneously inflammable liquids, yielding $Mg(OH)_2$ and CH_4 or C_2H_6 when decomposed by water.

Organo-mineral compounds similar to those which have been described are formed by other alcohol radicals.

It is not necessary that the chlorine atoms in the original inorganic type should be replaced by the same alcohol radical; thus, $Sn(CH_3)_2(C_2H_5)_2$ may be produced by the action of zinc methide upon $Sn(C_2H_5)_2Cl_2$; and $Sn(CH_3)_3C_2H_5$ is formed by zinc ethide with $Sn(CH_3)_3Cl$.

The fact that each element has an inherent power of holding in combination a definite number of radicals, elementary or compound, receives abundant illustration in the chemistry of organo-mineral compounds.

447. AMMONIA-DERIVATIVES, *formed upon the type of ammonia by the substitution of a compound radical for hydrogen.*—The organic compounds classed under this head are in many cases very nearly related

to the organo-mineral compounds, since such compounds as $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, $B(CH_3)_3$, are formed upon the types of PH_3, AsH_3, SbH_3, and BH_3, which are nearly allied to NH_3; but the strongly alkaline character of ammonia impresses special characters upon the bodies derived from it.

These may be divided into—

(1) *Amines*, formed by the substitution of alcohol-radicals for the hydrogen in ammonia, such as $NH_2.CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$.

(2) *Ammonium-bases*, formed by the substitution of alcohol-radicals for hydrogen in ammonia-hydrate, $NH_3.H_2O$, or NH_4HO, such as $N(CH_3)_4HO$.

(3) *Amides*, derived from ammonia by the substitution of acid-radicals for hydrogen, such as $NH_2(C_2H_3O)$, $NH(C_2H_3O)_2$, $N(C_2H_3O)_3$.

THE AMINES, OR COMPOUND AMMONIAS.—These are termed *primary*, *secondary*, or *tertiary* amines accordingly as one-third, two-thirds, or the whole of the hydrogen is replaced by an organic radical. Thus, if R' represent a monad radical (equivalent to H), R'' a diad (equivalent to H_2), and R''' a triad (equivalent to H_3), NH_2R' is a primary amine; NHR'_2 and NHR'' are secondary amines; and NR'_3, NR''', are tertiary amines. Amines are also distinguished as *monamines*, *di-amines*, and *tri-amines* accordingly as they contain one, two, or three atoms of nitrogen. Thus, NH_2R' is a primary monamine; N_2H_4R'' is a primary di-amine; and N_3H_6R''' is a primary tri-amine. NHR'_2 and NHR'' are secondary monamines; $N_2H_2R''_2$ and $N_2H_2R''R'_2$ are secondary di-amines; $N_3H_3R'''_2$, $N_3H_3R'''R'_3$, and $N_3H_3R'R''R'''$ are secondary tri-amines; NR'_3 and NR''' are tertiary monamines; $N_2R''_3$ and $N_2R''R'_4$ are tertiary di-amines; and $N_3R'''_3$ and $N_3R'''R'_6$ are tertiary tri-amines.

448. *Trimethylamine*, $N(CH_3)_3$, represents ammonia, NH_3, in which all the hydrogen has been replaced by methyl. It is obtained on a large scale by distilling the *vinasses* obtained in refining beet-root sugar, which corresponds to the molasses from cane-sugar, but is not fit for food. It contains sugar by the fermentation of which alcohols are obtained, and substances containing nitrogen,* which furnish ammonia and compound ammonias derived from the alcohols when distilled. By neutralisation with HCl, the hydrochlorides of ammonia, tri-ethylamine, &c., are obtained. The NH_4Cl, being less soluble, is crystallised out, and the $N(CH_3)_3.HCl$ is distilled with lime, when trimethylamine comes off as a gas which may be absorbed by water. The solution also contains dimethylamine, ethylamine, propylamine, and butylamine. It is used for converting KCl into K_2CO_3, by a process resembling the ammonia-soda process (p. 262), which depends on the fact that $NaHCO_3$ is less soluble in water than NH_4Cl; but $KHCO_3$ has about the same solubility as NH_4Cl, so that trimethylamine, whose hydrochloride is much more soluble, is substituted for ammonia.

To obtain pure trimethylamine, a strong solution of ammonia in alcohol is heated with methyl iodide for some hours, in a sealed tube immersed in boiling water. A series of reactions then takes place, resulting in the production of hydriodides of methylamine, $NH_2.CH_3$, dimethylamine, $NH(CH_3)_2$, trimethylamine, and tetramethylium iodide, $N(CH_3)_4I$. Let $Me = CH_3$ in the following equations:—

---

* Particularly *betaine* (*Beta vulgaris*, beet), or *trimethyl glycocine*, $C_2H_2(CH_3)_3NO_2$.

$$
\begin{aligned}
&(1)\ NH_3 + MeI = NH_2Me.HI;\\
&(2)\ 2NH_3 + 2MeI = NHMe_2.HI + NH_4I;\\
&(3)\ 3NH_3 + 3MeI = NMe_3.HI + 2NH_4I;\\
&(4)\ 4NH_3 + 4MeI = NMe_4I + 3NH_4I.
\end{aligned}
$$

The hydriodides of the three amines crystallise out on cooling, leaving the NMe_4I in solution. The hydriodides are distilled with KHO into a receiver cooled in ice, when a mixture of NMe_3, NMe_2H, and a little $NMeH_2$ is condensed, much of the last escaping as gas with the NH_3 from the NH_4I. The mixed amines are then digested with ethyl oxalate, when the NMe_3 is not acted on, and may be distilled off. The methylamine is converted into methyloxamide, and the dimethylamine into ethyl dimethyloxamate $(E = C_2H_5)$—

$$
\begin{aligned}
2NMeH_2 + C_2O_2(OE)_2 &= C_2O_2(NMeH)_2 + 2EOH;\\
NMe_2H + C_2O_2(OE)_2 &= C_2O_2.NMe_2.OE + EOH.
\end{aligned}
$$

Water at 0° dissolves the last-named compound, and leaves the methyloxamide undissolved. On distillation with potash, the methyloxamide yields potassium oxalate and methylamine; $C_2O_2(NMeH)_2 + 2KOH = C_2O_2(OK)_2 + 2NMeH_2$; and the ethyl dimethyloxamate yields potassium oxalate, dimethylamine, and alcohol—

$$C_2O_2.NMe_2.OE + 2KOH = C_2O_2(OK)_2 + NMe_2H + EOH.$$

Trimethylamine boils at 10° C.; it has a fish-like smell, is inflammable, and mixes easily with water. It forms salts by direct combination with acids, like ammonia. It is not unfrequently found in plants, as in the flowers of hawthorn, pear, and wild cherry, and in arnica and ergot of rye. It also occurs in the roe of the herring, and may be obtained by distilling herring-brine with lime. It is often found in the products of distillation of animal substances, together with amines containing other alcohol-radicals. Bones, when distilled, yield trimethylamine, methylamine, ethylamine, propylamine, and butylamine. The putrefaction of flour and other nitrogenous substances furnishes these ammonia-derivatives.

The hydrochlorate of trimethylamine is employed for making methyl chloride on the large scale. When its concentrated solution is heated to 260° C., it breaks up into methyl chloride, trimethylamine, and methylamine hydrochloride; $3NMe_3HCl = 2MeCl + 2NMe_3 + NMeH_2.HCl$. The gases are passed through hydrochloric acid to remove the bases, then over calcium chloride to absorb water, and the methyl chloride is condensed by pressure in iron cylinders. The methylamine hydrochloride is left after the more volatile products have escaped; it is dissolved in alcohol to free it from ammonium chloride, and distilled with potash to obtain methylamine.

449. *Methylamine*, NH_2CH_3, is a gas resembling ammonia, but more combustible and more soluble in water; in this it surpasses all gases, one volume of water dissolving 1150 volumes of methylamine. The solution is strongly alkaline. In its reactions with metallic salts it resembles ammonia, but it dissolves aluminium hydrate, and will not dissolve the hydrates of nickel and cobalt. Its behaviour with acids is similar to that of ammonia. When passed through a red-hot tube, it yields hydrocyanic acid, HCN, and ammonium cyanide, NH_4CN. Potassium converts it into potassium cyanide—

$$NH_2CH_3 + K = KCN + H_5.$$

Conversely, methylamine is formed by the action of nascent hydrogen on hydrocyanic acid; $HCN + H_4 = NH_2CH_3$. It is also produced by distilling methyl isocyanate with potash (see *Cyanogen*). Methylamine occurs in the fruit of *Mercurialis* (dog-mercury), a plant of the order *Euphorbiaceæ*. Several of the alkaloids yield it when distilled with potash.

Dimethylamine, $NH(CH_3)_2$, is a gas, condensing at 8° C., and resembling methylamine. It has been found in wood-spirit and in guano.

The ethyl-ammonias may be prepared by the action of ammonia on ethyl iodide, and may be separated from each other in the same way as the methyl-ammonias. They are prepared on a large scale by the action of ammonia upon the impure ethyl chloride obtained as a secondary product in the manufacture of chloral. This is heated for an hour in a closed vessel with a saturated alcoholic solution of ammonia. The volatile matters are then distilled off, and the hydrochlorides crystallised; on decomposing these with strong soda solution, the three ethylamines form an oily layer on the surface. They are separated as described under trimethylamine.

450. *Ethylamine*, $NH_2C_2H_5$, is an ammoniacal inflammable liquid, of sp. gr. 0.696, and boiling point 18°.7 C. It mixes with water in all proportions. It is a stronger base than ammonia, and dissolves alumina, though it does not easily dissolve cupric hydrate. Its salts may be regarded as salts of *ethyl-ammonium*, NH_3E. Thus the salt formed by neutralising ethylamine with hydrochloric acid may be written as *ethylamine hydrochloride*, $NH_2E.HCl$, or as *ethyl-ammonium chloride*, NH_3ECl, corresponding to ammonium chloride, NH_4Cl. The hydriodide, $NH_2E.HI$, is prepared by dissolving ethyl iodide in absolute alcohol, heating to the boiling point, passing dry NH_3 gas to saturation, and digesting until water no longer causes turbidity from separation of ethyl iodide.

Dichlorethylamine, $NCl_2C_2H_5$, is produced by the action of chlorine on aqueous ethylamine, or by distilling the hydrochloride with chloride of lime and water. It is a golden-yellow liquid, of very pungent smell, like chloropicrin (p. 540), insoluble in water, of sp. gr. 1.24, and boiling point 88° C. Zinc ethyl converts it into tri-ethylamine—

$$NCl_2C_2H_5 + Zn(C_2H_5)_2 = N(C_2H_5)_3 + ZnCl_2.$$

The corresponding iodine compound is a dark blue liquid decomposed by heat.

Di-ethylamine, $NH(C_2H_5)_2$, is also an ammoniacal liquid, boiling at 57°.5 C., and mixing easily with water. Unlike ethylamine, it does not dissolve zinc hydrate.

Nitroso-di-ethylamine, $N(C_2H_5)_2NO$, is di-ethylamine in which hydrogen has been replaced by nitrosyl, NO. It is obtained by distilling di-ethylamine hydrochloride with potassium nitrite and a little water. Di-ethylamine nitrite is first formed, and this is decomposed by distillation; $NHE_2.HNO_2 = NE_2NO + H_2O$.

Nitroso-di-ethylamine, or *di-ethyl nitrosamine*, is a yellow aromatic liquid, insoluble in water, of sp. gr. 0.95, and boiling point 177°. Nascent hydrogen reconverts it into di-ethylamine—

$$2NE_2NO + H_4 = 2NE_2H + H_2O + N_2O.$$

When dissolved in hydrochloric acid, and HCl gas passed into the solution, it yields nitrosyl chloride and di-ethylamine hydrochloride—

$$NE_2NO + 2HCl = NE_2H_2Cl + NOCl.$$

Tri-ethylamine, $N(C_2H_5)_3$, may be obtained by heating di-ethylamine with ethyl bromide; $N(C_2H_5)_2H + C_2H_5Br = N(C_2H_5)_3.HBr$; the crystallised hydrobromide thus obtained yields the triethylamine when distilled with potash. It differs from the other amines in having a pleasant smell, and being sparingly soluble in water. It boils at 89° C. Its reaction is strongly alkaline, and it resembles ammonia in its action upon metallic salts, except that it dissolves alumina, and scarcely dissolves silver oxide, which is readily soluble in ammonia.

The other alcohol radicals, propyl, butyl, amyl, &c., also produce amines by replacing the hydrogen in NH_3. It is not necessary that two or three atoms of H be replaced by the same radical; we may have *mixed amines*, such as *methyl-ethylamine*, $NH.CH_3.C_2H_5$, obtained by the action of ethyl iodide on methylamine; and if this be acted on by amyl iodide, *methyl-ethyl-amylamine*, $N.CH_3.C_2H_5.C_5H_{11}$, is produced.

451. *To ascertain whether an amine is primary, secondary, or tertiary*, heat its hydrochloride with silver nitrite. A primary amine yields the corresponding alcohol—

$$NH_2.C_2H_5.HCl + AgNO_2 = C_2H_5.OH + AgCl + H_2O + N_2;$$

a secondary amine yields a nitroso-amine—

$$NH(C_2H_5)_2HCl + AgNO_3 = AgCl + H_2O + N(C_2H_5)_2.NO;$$

a tertiary amine is not decomposed.

Another method of investigating the constitution of an amine, is to heat its alcoholic solution with methyl iodide in a sealed tube; a tertiary amine will yield a substituted ammonium iodide by direct union with methyl iodide; $N(C_2H_5)_3 + CH_3I = N(C_2H_5)_3.CH_3I$; a secondary amine will yield an ammonium iodide containing two methyl groups; $NH(C_2H_5)_2 + 2CH_3I = HI + N(C_2H_5)_2(CH_3)_2I$; a primary amine will yield an ammonium iodide containing three methyl groups—

$$NH_2(C_2H_5) + 3CH_3I = N(C_2H_5)(CH_3)_3I + 2HI.$$

452. *Ethene-diamine*, or *ethylene-diamine*, $N_2H_4(C_2H_4)''$, is formed by the action of ethene dibromide or dichloride upon an alcoholic solution of ammonia at 100° C.; $2NH_3 + C_2H_4Cl_2 = N_2H_4.C_2H_4.2HCl$. Crystals of the hydrobromide or hydrochloride are obtained, which yield the diamine when distilled with potash. It distils over in combination with H_2O, which can only be removed by distilling with sodium. Ethene-diamine has very little odour of ammonia, dissolves in water, giving an alkaline solution, and boils at about 120° C. It is a di-acid base, that is, it is equivalent to two molecules of NH_3 in its relations to acids. By the action of ethyl iodide, the hydrogen of the ammonia type may be replaced by ethyl, yielding *diethyl-ethene-diamine*, $N_2(C_2H_4)''H_2(C_2H_5)_2$, and *tetrethyl-ethene-diamine*, $N_2(C_2H_4)''(C_2H_5)_4$.

Ethene-diamine, when acted on by nitrous anhydride, is converted into ethene oxide; $N_2H_4.C_2H_4 + N_2O_3 = 2N_2 + 2H_2O + C_2H_4.O$. A very remarkable reaction, furnishing ethene-diamine, occurs when cyanogen is passed into hydrochloric acid while acting on metallic tin; $Sn_4 + 10HCl + (CN)_2 = 4SnCl_2 + N_2H_4.C_2H_4.2HCl$.

Diethene-diamine, $N_2H_2(C_2H_4)''_2$, and *triethene-diamine*, $N_2(C_2H_4)''_3$, are formed, together with ethene-diamine, by the action of ethene-dibromide on alcoholic ammonia. A mixture of the three diamines is obtained when the hydrobromides are distilled with potash, and they may be separated by fractional distillation, ethene-diamine boiling at 120° C., diethene-diamine at 170° C., and triethene-diamine at 210° C. By means of ethyl iodide, the ammonia-hydrogen of diethene-diamine may be replaced by ethyl, producing *diethyl-diethene-diamine*—

$$N_2(C_2H_5)_2(C_2H_4)_2.$$

Diethene-triamine, $N_3H_5(C_2H_4)''_2$, and *triethene-triamine*, $N_3H_3(C_2H_4)_3$, are also products of the action of ethene-dibromide upon ammonia. They are liquids with high boiling points, acting as tri-acid bases, but capable of forming mon-acid and di-acid, as well as tri-acid, salts. By the joint action of ethylamine and ammonia on ethene-dibromide, *diethene-diethyl-triamine*, $N_3H_3(C_2H_4)''_2(C_2H_5)_2$, has been obtained.

453. THE AMMONIUM BASES. *Tetramethylium hydrate*, $N(CH_3)_4.OH$, is prepared by decomposing the iodide with silver hydrate—

$$NMe_4I + AgHO = NMe_4.OH + AgI.$$

The tetramethylium iodide is obtained by heating an alcoholic solution of ammonia with an excess of methyl iodide in a sealed tube to 100° C. for some time; $4NH_3 + 4MeI = NMe_4I + 3NH_4I$. The ammonium iodide, being nearly insoluble in alcohol, crystallises out, and the tetramethylium iodide is obtained in prismatic crystals by evaporating the solution, and may be purified by crystallisation from water, in which it is rather sparingly soluble. When decomposed, as above, by silver hydrate, the solution filtered from the AgI, when evaporated *in vacuo*, yields a crystalline deliquescent mass of tetramethylium hydrate, which acts like a caustic alkali, and absorbs CO_2 from the air.

When heated, it yields methyl alcohol and trimethylamine—

$$NMe_4OH = NMe_3 + MeOH.$$

Its salts are not decomposed by potash, even on boiling; this forms a point of *distinction between the salts of amines and ammonium bases.*

Tetrethylium hydrate, $N(C_2H_5)_4.OH$, is prepared like the methyl compound, which it much resembles, but crystallises rather more easily. In its chemical behaviour, it is very similar to potassium hydrate, but it produces, in chromic salts, a precipitate of chromic hydrate, which does not dissolve in excess. Moreover, when heated to 100° C., it does not yield alcohol, but ethene, water, and tri-ethylamine; $N(C_2H_5)_4.OH = C_2H_4 + H_2O + N(C_2H_5)_3$. If it be heated with ethyl iodide, alcohol and *tetrethylium iodide* are formed; $NE_4OH + EI = EOH + NE_4I$. The iodide may be obtained by the combination of $N(C_2H_5)_3$ with C_2H_5I, just as NH_4I is formed by NH_3 and HI, the combination producing heat. Tetrethylium iodide is also prepared, like the methyl compound, by heating alcoholic ammonia, in a sealed tube, to 100° C., with excess of ethyl iodide. It crystallises in cubes like the alkaline iodides, which become brown, when exposed to air, from the formation of *tetrethylium triodide*, NE_4I_3. Tetrethylium iodide is very soluble in alcohol and in water, but is insoluble in solution of potash, which precipitates it from the aqueous solution, but without decomposing it. When heated, tetrethylium iodide undergoes dissociation, like ammonium chloride, yielding ethyl iodide, which distils over, and is followed by triethylamine, these afterwards combining to reproduce the iodide.

The ammonium bases form salts with acids in the same way as the alkaline hydroxides; thus, $NE_4OH + HNO_3 = NE_4NO_3 + H_2O$; $2NE_4OH + H_2SO_4 = (NE_4)_2SO_4 + 2H_2O$.

The 4 atoms of hydrogen in the original $NH_4.OH$ type admit of being replaced by different radicals; thus, *trimethyl-ethylium iodide*, $N(C_2H_5)(CH_3)_3I$, is obtained by acting on trimethylamine with ethyl iodide; and *methyl-diethyl-amylium iodide*, $N(C_5H_{11})(C_2H_5)_2CH_3I$, is formed when amyl iodide acts on methyl-diethylamine, $N(C_2H_5)_2.CH_3$.

454. *Allylamine*, $NH_2.C_3H_5$, is a primary monamine formed by the action of allyl iodide upon ammonia, or by acting on mustard oil, dissolved in alcohol, with zinc and hydrochloric acid; $C_3H_5.NCS + Zn + 3HCl = NH_2.C_3H_5.HCl + ZnCl_2 + CS$. By distilling the hydrochlorate with potash, allylamine is obtained as an ammoniacal liquid of sp. gr. 0.86, and boiling at 58° C. It is soluble in water, and has strong basic properties. The chief product of the action of allyl iodide upon ammonia is *tetrallylium iodide*, $N(C_3H_5)_4I$, which yields the ammonium base, $N(C_3H_5)_4.OH$, *tetrallylium hydrate*, when decomposed by silver hydrate. This is a

caustic alkaline base, which, when distilled, yields *triallylamine*, $N(C_3H_5)_3$, a liquid base, boiling at 150° C.

Ethyl-allylamine, $N.C_3H_5.C_2H_5.H$, and *diethyl-allylamine*, $N.C_3H_5(C_2H_5)_2$, have been obtained by heating allylamine with ethyl iodide. Trichlorhydrin (the hydrochloric ether of glycerin), $C_3H_5Cl_3$, when heated with ammoniacal alcohol, yields dichlorallylamine, $NH(C_3H_4Cl)_2$, also a volatile base.

Benzylamine, $NH_2.C_7H_7$, a liquid base, boiling at 183° C.; *dibenzylamine*, $NH(C_7H_7)_2$, also liquid, boiling at 300° C.; and *tribenzylamine*, $N(C_7H_7)_3$, a crystalline solid, are formed by the action of benzyl chloride, C_7H_7Cl, upon ammonia.

455. *Phenylamine*, or *aniline*, or *amidobenzene*, $NH_2.C_6H_5$, is prepared from nitrobenzene, $C_6H_5.NO_2$, by reducing it with metallic iron in conjunction with acetic or hydrochloric acid.

On the large scale, the operation is conducted in a cast-iron retort provided with an agitator and condenser. Five parts of fine cast-iron filings, 8 parts of water, and 2 parts of hydrochloric acid are introduced into the retort, and 20 parts of nitrobenzene are allowed to flow slowly in, with constant stirring. Steam is blown into the retort through the hollow agitator, and more iron filings are gradually added, so as to keep up a moderate action, until about 25 parts of iron have been added in all. Some of the nitrobenzene volatilises, and runs back from a vertical condenser. When the reaction is terminated, slaked lime is added to combine with the hydrochloric acid, and high-pressure steam is blown in, when aniline and water distil over, the former sinking to the bottom, and the water, which retains a little aniline, being used to furnish steam for the next operation. The aniline is purified by distillation, and the iron residues are sent to the blast furnaces (Roscoe and Schorlemmer).

The reactions in the preparation may be stated thus—

(1) $C_6H_5.NO_2 + Fe_3 + 6HCl = C_6H_5.NH_2 + 3FeCl_2 + 2H_2O$;
(2) $C_6H_5.NO_2 + 6FeCl_2 + 6HCl = C_6H_5.NH_2 + 3Fe_2Cl_6 + 2H_2O$.

The process requires care, because, if the iron filings be added too quickly, the action becomes too violent, and benzene and ammonia are produced; $C_6H_5.NO_2 + H_8 = C_6H_5.H + NH_3 + 2H_2O$.

On the small scale, tin is more convenient than iron. Granulated tin is placed in a retort with inverted condenser, and covered with strong HCl; nitrobenzene is added in small portions, and when the action has moderated, the mixture is boiled till all the nitrobenzene has disappeared; the liquid is decanted from the excess of tin, when it deposits, on cooling, a crystalline compound of aniline hydrochloride with stannous chloride; $(NH_2.C_6H_5.HCl)_2.SnCl_2.2Aq$. By distilling this with excess of potash or soda, the aniline is set free.

If iron be employed, acetic acid should be used, suitable proportions being 1 part of nitrobenzene, 1 part of strong acetic acid, and 1.2 part of iron filings.

Nitrobenzene may also be converted into aniline by dissolving it in alcohol, saturating the solution with ammonia gas, then with H_2S gas repeatedly, as long as the latter is acted on; $C_6H_5NO_2 + 3H_2S = C_6H_5NH_2 + 2H_2O + S_3$. The liquid is decanted from the sulphur, and the alcohol and ammonium sulphide distilled off in a water-bath; the mixture of aniline and any unaltered nitrobenzene is treated with HCl, which dissolves only the aniline: this may be liberated by distillation with potash.

Since commercial benzene contains toluene and other hydrocarbons, the nitrobenzene and aniline prepared from it will contain toluidine and other bases. To purify it, the crude aniline is boiled with glacial acetic acid, in a flask with a reversed condenser, when it is converted into *acetanilide*, $NH.C_6H_5.C_2H_3O$. This is distilled, washed with carbon disulphide, and recrystallised from water till its melting point is 112° C., when pure aniline may be obtained from it by boiling with caustic soda—

(1) $NH_2.C_6H_5 + C_2H_3O.OH = NH.C_6H_5.C_2H_3O + HOH$;
(2) $NH.C_6H_5.C_2H_3O + NaOH = NH_2.C_6H_5 + NaO.C_2H_3O$.

Aniline was orginally obtained by distilling indigo, either alone or with caustic alkalies, and was named from *anil*, the Portuguese name of indigo. It is also found in coal tar, and in the products of distillation of bones and peat.

Properties of aniline.—Colourless when pure, but generally of a yellow or even brown colour, having a characteristic rather ammoniacal smell: sp. gr. 1.03, and boiling point 184° C. When shaken with water, it appears almost insoluble, but the water takes up about $\frac{1}{30}$th of its weight of aniline, and the latter takes up about $\frac{1}{20}$th of its weight of water. It is easily soluble in alcohol and ether, and the latter may be employed to collect it from an aqueous solution. Its basic properties are stronger than those of ammonia, but it has no alkaline reaction. Most of its salts crystallise easily. The hydrochloride, $NH_2.C_6H_5.HCl$, is commercially known as *aniline-salt*. The oxalate, $(C_6H_7N)_2.H_2C_2O_4$, is rather sparingly soluble in water.

Aniline has the rare property of dissolving indigo.

Many oxidising agents produce intensely coloured products with aniline. The usual test for it is solution of chloride of lime (bleaching-powder), which gives a purple-violet colour, changing to brown.

Aniline, being a primary monamine, may be converted into secondary and tertiary amines by replacing the hydrogen of the amidogen by other radicals. Thus, *methylaniline*, $NH.CH_3.C_6H_5$, and *dimethylaniline*, $NC_6H_5(CH_3)_2$, are obtained by the action of methyl iodide on aniline, or by heating methyl alcohol with aniline hydrochloride, in a closed vessel, to 250° C., when the hydrochlorides of the methyl bases and water are produced. Methyl aniline is also prepared on a large scale by the action of methyl chloride on a heated mixture of aniline and caustic soda; $2CH_3Cl + NH_2C_6H_5 + 2NaHO = NC_6H_5(CH_3)_2 + 2NaCl + 2H_2O$. They are liquids boiling at about 190° C., and used in the manufacture of certain aniline dyes. *Ethyl-methylaniline*, $N.C_6H_5.C_2H_5.CH_3$, and other similar amines have been obtained.

456. *Phenylaniline*, or *diphenylamine*, $NH(C_6H_5)_2$, is a secondary monamine obtained by heating aniline hydrochloride with aniline to 250° C., in a closed vessel from which the NH_3 is allowed to escape from time to time—

$$NH_2C_6H_5.HCl + NH_2C_6H_5 = NH(C_6H_5)_2 + NH_3.HCl;$$

the excess of aniline employed decomposes the ammonium chloride, so that a mixture of aniline hydrochloride and diphenylamine is left; on adding water, the latter is left undissolved. It is a crystalline solid, soluble in alcohol and ether, and having feeble basic properties. When acted on by nitric acid, three atoms of the phenyl hydrogen are replaced by NO_2, producing *trinitrodiphenylamine*, $NH(C_6H_2(NO_2)_3)_2$, in which the remaining ammonia hydrogen may be replaced by NH_4, the resulting compound, $N.NH_4.(C_6H_2(NO_2)_3)_2$, being used as an orange dye, ***aurantin***.

Diphenylamine is used as a delicate test for nitric acid, with which it gives a deep blue colour in acid solutions, from the production of *dinitrodiphenylamine*, $NH(C_6H_3(NO_2)_2)_2$.

By heating diphenylamine hydrochloride with methyl alcohol in a closed vessel, *methyl-diphenylamine*, $NCH_3(C_6H_5)_2$, is obtained. It is a feebly basic liquid, boiling at 282° C., used in the manufacture of blue colours.

The ammonia-hydrogen in aniline may be evolved by dissolving potassium in the base, when $NHK.C_6H_5$ and $NK_2C_6H_5$ are produced. By acting on the latter with phenyl bromide, the tertiary amine, *triphenylamine*, $N(C_6H_5)_3$, is produced—

$$NK_2C_6H_5 + 2C_6H_5Br = N(C_6H_5)_3 + 2KBr.$$

This compound is not basic; it is insoluble in water, but may be crystallised from ether.

457. When aniline is acted on by ethene dibromide, it yields the secondary diamine, $N_2H_2(C_6H_5)_2(C_2H_4)''$, called *ethene-diphenyl-diamine*, and the tertiary diamine, $N_2(C_6H_5)_2(C_2H_4)''_2$, or *diethene-diphenyl-diamine*: they are also known as ***ethene-aniline*** and ***diethene-aniline***, and are crystalline solids.

Phenylene-diamine, or *diamidobenzene*, $N_2H_4(C_6H_4)''$, is prepared by reducing dinitrobenzene, $C_6H_4(NO_2)_2$, with iron filings and acetic acid, just as phenylamine, $NH_2.C_6H_5$, is prepared from nitrobenzene, $C_6H_5.NO_2$, the two nitroxyl groups being reduced to two amidogen groups. It a crystalline di-acid base. When dinitrobenzene is reduced by ammonium hydrosulphide (p. 579), the first product is a yellow crystalline body called *nitraniline*, or *nitrophenylamine*, $NH_2.C_6H_4.NO_2$; it is a very weak base. *Dinitraniline*, $NH_2.C_6H_3(NO_2)_2$, is an indifferent body, and *trinitraniline*, $NH_2.C_6H_2(NO_2)_3$, has weak acid properties.

Chloraniline, $NH_2.C_6H_4Cl$, may be obtained by reducing *chloronitrobenzene*, $C_6H_4Cl.NO_2$, with tin and hydrochloric acid. It is a liquid with feeble basic properties. The chloronitrobenzene is prepared by the action of nitric acid on *chlorobenzene*, C_6H_5Cl, a fragrant liquid obtained by heating benzene to 150° C. with sulphuryl chloride: $C_6H_6 + SO_2Cl_2 = C_6H_5Cl + HCl + SO_2$. *Dichloraniline* $NH_2.C_6H_3Cl_2$, *trichloraniline*, $NH_2.C_6H_2Cl_3$, *tetrachloraniline*, $NH_2.C_6HCl_4$, and *pentachloraniline*, $NH_2.C_6Cl_5$, have been obtained, but the introduction of the chlorous radical has destroyed the basic character of the aniline-type. The corresponding bromine compounds have been obtained; *tribromaniline* is precipitated when bromine water is added to an aqueous solution of aniline. *Mono-*, *di-*, and *tri-iodaniline* are also known.

458. *Azobenzene*, $C_6H_5N : NC_6H_5$, a representative of the class of *azo-compounds*, is formed from aniline by certain processes of moderate oxidation which remove the H_2 of the amidogen from two molecules of aniline, leaving the residues to combine and produce a molecule of azobenzene; $2NH_2C_6H_5 + O_2 = 2H_2O + (C_6H_5N)_2$. It is formed when aniline hydrochloride is oxidised with potassium permanganate. Since aniline is obtained by the reduction of nitrobenzene, azobenzene might be expected to be produced in the same way, and accordingly, if an alcoholic solution of nitrobenzene be treated with sodium amalgam, or with zinc-dust and NaHO, the nascent hydrogen converts the nitrobenzene into azobenzene; $2C_6H_5NO_2 + H_8 = (C_6H_5N)_2 + 4H_2O$. It is readily obtained by dissolving nitrobenzene in alcohol, adding an equal weight of potassium hydrate, and distilling, when the alcohol is oxidised to acetic acid, and the nitrobenzene is reduced to azobenzene. At the end of the distillation, it comes over as a dark-red oil, which solidifies after a time to a crystalline mass, fusible at 66° C., and boiling at 293° C.; it is insoluble in water, but may be crystallised from alcohol or ether in beautiful red tables resembling potassium dichromate.

Azobenzene (formerly called *azobenzide*) is obtained at the end of the distillation in the preparation of aniline from nitrobenzene (p. 579) by the action of iron. The hydrogen in azobenzene admits of replacement by chlorous radicals, such as Cl, NO_2, and HSO_3, forming numerous substitution-products, most of which are highly coloured. When azobenzene is dissolved in acetic acid and oxidised by chromic acid, it is converted into *azoxybenzene*, $C_6H_5N.O.NC_6H_5$, which is the first product of the reduction of nitrobenzene by alcohol and potash. It crystallises in yellow needles fusing at 36° C., insoluble in water, but soluble in alcohol.

Hydrazobenzene, $C_6H_5HN.NHC_6H_5$, is the compound intermediate between azobenzene, $C_6H_5N.NC_6H_5$, and a double aniline molecule, $(C_6H_5.H_2N)_2$. It is formed when nascent hydrogen combines with azobenzene, and may be prepared by dissolving azobenzene in alcohol, passing ammonia gas, and afterwards H_2S till the solution is colourless. On adding water, the hydrazobenzene is precipitated, and may be crystallised from alcohol. It forms colourless tables, which become orange in air, from production of azobenzene, and have the odour of camphor. Its formation is explained by the equation—

$$C_6H_5N.NC_6H_5 \quad + \quad H_2S \quad = \quad C_6H_5HN.NHC_6H_5 \quad + \quad S.$$

A convenient method of converting azobenzene into hydrazobenzene is to boil its alcoholic solution with zinc-dust until it is colourless.

When heated, hydrazobenzene is decomposed into azobenzene and aniline—

$$2(C_6H_5HN.NHC_6H_5) \quad = \quad C_6H_5N.NC_6H_5 \quad + \quad 2(C_6H_5.H_2N).$$

When dissolved in hydrochloric or sulphuric acid, it is converted into an isomeric base, $NH_2.H_4C_6\,C_6H_4.NH_2$, known as *benzidine*, or *diamido-diphenyl*, which crystallises in silvery plates from hot water, and is precipitated from its hydrochloride by ammonia.

459. *Diazobenzene* is the name given by its discoverer to the product of the action of nitrous acid upon aniline, because he regarded it as benzene, C_6H_6, in which two nitrogen atoms replaced two hydrogen atoms, and the apparently appropriate name, dinitrobenzene, had already been conferred upon $C_6H_4(NO_2)_2$, resulting from the action of nitric (and sulphuric) acid on benzene. The French name for nitrogen, *azote*, was therefore brought into use.

Diazobenzene nitrate, $C_6H_5N_2.NO_3$, is prepared by passing N_2O_3 gas into a thin paste of aniline nitrate and water, cooled by ice and salt, until potash no longer precipitates aniline. A brown product is filtered off, and alcohol added to the filtrate, when the nitrate separates in colourless needles. These are soluble in water, but insoluble in ether, and sparingly soluble in alcohol. When heated to 90° C., it detonates with extreme violence, and a blow detonates it like mercuric fulminate; it has been proposed for use in detonating primers.

The theory of its production is important on account of its general bearing. The old view regarded it as formed by the substitution of an atom of triad nitrogen for three hydrogen atoms in aniline, as in the equation, $C_6H_7N.HNO_3$ (aniline nitrate) + HNO_2 (nitrous acid) = $C_6H_4N_2.HNO_3$ (diazobenzene nitrate); here, the diazobenzene is represented as benzene, C_6H_6, in which H_2 have been replaced by N_2. The reactions of the diazobenzene salts, however, indicate the presence of the phenyl group, C_6H_5; thus, when boiled with water, the nitrate evolves phenol, known by the smell—

$$C_6H_5N_2.NO_3 + H_2O = C_6H_5.OH + N_2 + HNO_3;$$

when boiled with alcohol, it yields benzene and aldehyd—

$$C_6H_5N_2.NO_3 + C_2H_5.HO = C_2H_4O + C_6H_5.H + N_2 + HNO_3;$$

boiled with hydrochloric acid, it gives chlorobenzene—

$$C_6H_5N_2.NO_3 + HCl = C_6H_5Cl + N_2 + HNO_3.$$

Accordingly, modern chemists regard the substitution of N''' for H_3 as having taken place in an NH_3 group, the aniline nitrate being represented as phenyl-ammonium nitrate; $C_6H_5.NH_3.NO_3 + HNO_2 = C_6H_5N(N).NO_3 + 2H_2O$. The general mode of action of nitrous acid upon bodies containing the NH_2 group consists in substituting $(OH)'$ for $(NH_2)'$; thus, $H.NH_2 + NO.OH = H.OH + H_2O + N_2$; in a similar way, aniline is converted into phenol by the action of nitrous acid; $C_6H_5.NH_2 + NO.OH = C_6H_5.OH + H_2O + N_2$. But when a salt of an aromatic amine is acted on by nitrous acid, no nitrogen is evolved, the N of the HNO_2 being exchanged for H_3 from the amine, and H from the acid, thus linking the residues to form a new molecule—

$$C_6H_5.NH_2.HNO_3 + HNO_2 = C_6H_5N.N.NO_3 + 2H_2O.$$

The *diazo-reaction*, as it is termed, is of great importance in investigating the constitution of organic compounds, especially of those derived from benzene, for, by treatment with nitrous acid, a nitro-substitution product may be converted into—(1) the amido-compound, *e.g.*, nitrobenzene, $C_6H_5.NO_2$, into aniline, $C_6H_5.NH_2$; (2) the diazo-compound, *e.g.*, aniline into diazobenzene, $C_6H_5N_2$; (3) the hydroxide, *e.g.*, diazobenzene into phenol, $C_6H_5.OH$; (4) the halogen-derivative, *e.g.*, diazobenzene into chlorobenzene, C_6H_5Cl; and (5) the hydrocarbon itself, *e.g.*, diazobenzene into benzene, $C_6H_5.H$.

By decomposing diazobenzene nitrate with potash, the compound $C_6H_5N_2.OK$ is obtained, in which the potassium may be replaced by other metals, producing unstable and sometimes explosive compounds. By acting on the potassium compound with acetic acid, *diazobenzene hydroxide*, $C_6H_5N_2.OH$, is obtained as a very unstable liquid.

Diazobenzene chloride, $C_6H_5N_2.Cl$, is prepared by dissolving aniline in diluted HCl, cooling the solution, and adding sodium nitrite till the smell of nitrous vapour is perceptible. It is known only in solution, and is employed in the preparation of some of the aniline colours. When it is acted on by aniline, it yields *amido-azobenzene*, $C_6H_5N.N.C_6H_4.NH_2$, or *aniline yellow*—

$$C_6H_5N_2.Cl + C_6H_5.NH_2 = C_6H_5N.NC_6H_4NH_2 + HCl.$$

Diazo-amidobenzene, $C_6H_5N_2.NH.C_6H_5$, is a yellow crystalline body formed by the action of N_2O_3 upon a cold alcoholic solution of aniline—

$$2(C_6H_5.NH_2) + HNO_2 = C_6H_5N_2.NHC_6H_5 + 2H_2O.$$

460. *Diamido-azobenzene*, $C_6H_5N.N.C_6H_3(NH_2)_2$, is produced by the action of phenylene-diamine, on diazobenzene chloride—

$$N_2H_4(C_6H_4)'' + C_6H_5N_2Cl = C_6H_5N.N.C_6H_3(NH_2)_2 + HCl.$$

The hydrochloride is used as an orange dye under the name of *chrysoidin*.

Triamido-azobenzene, $C_6H_4(NH_2).N.N.C_6H_3(NH_2)_2$, is prepared by the action of sodium nitrite on a cold dilute solution of phenylene-diamine in hydrochloric acid; $2N_2H_4(C_6H_4)'' + HNO_2 = C_6H_4(NH_2).N_2.C_6H_3(NH_2)_2 + 2H_2O$. The hydrochloride is used for dyeing wool brown (*phenylene brown*).

The solution of phenylene-diamine hydrochloride produces a yellow or brown colour in extremely dilute solutions of nitrites.

Nearly all the azo-compounds which contain either the HO or the NH_2 group may be used as dyes, though many of them are very fugitive.

Dimethylamido-azobenzene, $C_6H_5N_2.C_6H_4N(CH_3)_2$, is obtained by the action of methyl iodide on amido-azobenzene; it is a red crystalline base, which is converted by fuming sulphuric acid into dimethylamido-azobenzene sulphonic acid, $C_6H_4(SO_3H)N_2.C_6H_4.N(CH_3)_2$, precipitated by water, and crystallising in violet plates.

Ammonium dimethylamido azobenzene sulphonate, $C_6H_4(SO_3NH_4)N_2.C_6H_4.N(CH_3)_2$, is used as a red dye under the names *Tropæolin*[*] *D* and *Orange III*. It is sometimes used in analysis instead of litmus, as its orange-coloured aqueous solution becomes light red with a trace of free acid.

461. *Amidobenzene sulphonic acid*, or *sulphanilic acid*, or *aniline sulphonic acid*, $C_6H_4(SO_3H).NH_2$, is obtained by dissolving aniline in half its weight of sulphuric acid, mixed with water, evaporating to dryness, adding a similar quantity of sulphuric acid, mixing to a paste with sand, drying up, and crystallising from boiling water. When this is dissolved in soda, mixed with sodium nitrite, and poured into cooled sulphuric acid, *di-azobenzene sulphonic acid*, $C_6H_4SO_3N_2$, is precipitated; $C_6H_4.SO_3H.NH_2 + HNO_2 = C_6H_4SO_3N_2 + 2H_2O$. By acting on this with diphenylamine, $NH(C_6H_5)_2$, a steel-blue crystalline acid is obtained, which is *phenylamido-azobenzene sulphonic acid*, $C_6H_4.SO_3H.N_2.C_6H_4NH.C_6H_5$. The potassium salt of this acid is sold as *Tropæolin OO* or *Orange IV*, and used as a golden yellow dye. It is a good substitute for litmus, as its solution is changed to bright red by the stronger acids, but is not affected by CO_2 or H_2S.

By heating the above sulphonic acid with aniline, *azodiphenyl blue*, or *induline*, $C_{18}H_{15}N_3$, is obtained, together with aniline sulphonic acid—

$$C_6H_4.SO_3H.N_2.C_6H_4NH.C_6H_5 + NH_2.C_6H_5 = C_{18}H_{15}N_3 + C_6H_4(SO_3H).NH_2.$$

Commercial induline is the hydrochloride, which forms crystals nearly insoluble in water, but dissolved by alcohol to a blue solution.

Nigraniline, or *aniline black*, $C_{30}H_{25}N_5$, is a di-acid base of uncertain constitution, obtained as an amorphous precipitate by the action of potassium permanganate or chlorate upon aniline salts. In calico-printing, a mixture of sodium chlorate, aniline hydrochloride, and a little ammonium vanadate is employed; the latter appears to act as a carrier of oxygen.

Safranine, or *aniline pink*, $C_{18}H_{14}N_4.HCl$, is obtained by oxidising a mixture of aniline hydrochloride and diamidobenzene hydrochloride with potassium dichromate; $2NH_2C_6H_5 + C_6H_4(NH_2)_2 + O_4 = C_{18}H_{14}N_4 + 4H_2O$.

When aniline black is boiled with tin and HCl, it is converted into *diamido-diphenylamine*, $NH(C_6H_4.NH_2)_2$, which may be crystallised from water. If this be heated with sulphur, and the product oxidised by ferric chloride, it yields *thionine hydrochloride*, or *Lauth's violet*, $C_{12}H_9N_3S.HCl$, which crystallises in beetle-green needles slightly soluble in cold water, and dissolving when heated to a violet solution in which ammonia gives a black crystalline precipitate of thionine.

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[*] From the flowers of *Tropæolum majus*, the garden *Nasturtium*.

Tetramethyl-thionine chloride, $C_{12}H_6(CH_3)_4N_3SCl$, or *methylene blue*, is prepared from dimethylaniline hydrochloride by treating it with sodium nitrite and afterwards with hydrosulphuric acid. The excess of the latter is oxidised by potassium dichromate, the solution saturated with NaCl, and $ZnCl_2$ added, which forms an insoluble compound with the chloride; the latter may be obtained pure by recrystallisation from hot dilute HCl. It forms bronze-green crystals, which dissolve in cold water to a fine blue liquid employed in dyeing, being fixed on cotton with a mordant of antimony tannate. It has also been found very useful as a staining material for microscopic physiology.

The production of *methylene white*, $C_{12}H_7(CH_3)_4N_3S$, by the action of reducing agents has led to the use of methylene blue for measuring the reducing power of different portions of the body. The formation of the blue is one of the most delicate tests for H_2S in solution; the liquid to be tested is mixed with excess of HCl, a little dimethyl-paradiamido-benzene sulphate added, followed by a drop of ferric chloride.

Tetramethyl-thionine hydroxide, $C_{12}H_6(CH_3)_4N_3S.OH$, is an ammonium base obtained by decomposing the chloride with silver hydrate.

462. *Toluidine*, $NH_2.C_7H_7$, or *amido-toluene*, $C_6H_4.CH_3.NH_2$, is isomeric with methyl-aniline. It is prepared by reducing nitrotoluene, just as aniline is prepared from nitrobenzene. There are three isomeric toluidines known: *ortho-*, *meta-*, and *para-toluidine*, obtained, respectively, from *ortho-*, *meta-*, and *para-nitrotoluenes*. Orthotoluidine is a liquid resembling aniline, of sp. gr. 1.003, and boiling point 199°.5 C. It becomes pink in air. Chloride of lime gives it a brown colour, which is changed to red by acids. The *aniline-oil* of commerce always contains toluidine, so that it gives a brown colour with chloride of lime, as well as the violet due to aniline. By shaking with ether, the toluidine brown is removed, and becomes pink when the ethereal layer is shaken with acetic acid. Metatoluidine is a liquid of sp. gr. 0.998, and boiling at 197° C. Paratoluidine, which is the chief constituent of commercial toluidine, is a crystalline solid, fusing at 45° C. and boiling at 198° C. It is sparingly soluble in water, and is feebly alkaline; alcohol and ether dissolve it. Its basic properties are weak. Its oxalate is insoluble in ether, which dissolves orthotoluidine oxalate. When methylaniline hydrochloride is heated to 350° C., it is converted into the isomeric paratoluidine hydrochloride; $NH.CH_3.C_6H_5.HCl = NH_2.C_6H_4.CH_3.HCl$.

Mauvéine, $C_{27}H_{24}N_4$, is a base of unknown constitution, formed when commercial aniline containing toluidine is converted into sulphate, dissolved in water, and oxidised by enough potassium dichromate to form K_2SO_4; after some hours, a black precipitate separates, which is washed, dried, purified by digesting with benzene, and boiled with alcohol; on evaporating the solution, a bronze-coloured mass of mauvéine sulphate is left, which is soluble in hot water. This was the first discovered of the now numerous aniline dyes, and was named, after its discoverer, *Perkin's purple*. The base appears to result from the oxidation of a mixture of one molecule of aniline and three of toluidine—

$$C_6H_7N + 3C_7H_9N + O_5 = 5H_2O + C_{27}H_{24}N_4.$$

The sulphate is $(C_{27}H_{24}N_4)_2H_2SO_4$. By dissolving it in boiling water and adding potash, mauvéine is precipitated in black shining crystals, soluble in alcohol, with a violet colour changed to blue by strong acids, and to purple by absorption of CO_2. The acid carbonate, $C_{27}H_{24}N_4.H_2CO_3$, is obtained in bronze-green prisms by passing CO_2 through a hot alcoholic solution.

Rosaniline, $C_{20}H_{19}N_3$, is another base of obscure constitution, obtained by the action of oxidising agents upon the mixture of aniline and toluidine which composes the aniline of commerce, the equation for its formation being probably—

$$C_6H_7N + 2C_7H_9N + O_3 = 3H_2O + C_{20}H_{19}N_3.$$

Its salts are used in dyeing, under the names of *aniline red*, *magenta*, *fuchsine*, *roseine*, *azaleine*, &c., but the base itself is colourless.

To prepare it, 5 parts of *aniline-oil* and 6 parts of commercial arsenic acid, and a little water, are heated to about 130° C., for about six hours. The bronze-green mass is boiled with water, and a slight excess of soda added, which precipitates the rosaniline; this is washed, and dissolved in acetic acid, which gives a red solution, from which *rosaniline acetate*, $C_{20}H_{19}N_3.HC_2H_3O_2$, may be crystallised in splendid bronze-green rhombic octahedra. If this be dissolved in hot water, mixed with ammonia, and filtered rapidly, the solution deposits colourless plates of $C_{20}H_{19}N_3.H_2O$, sparingly soluble in water, but yielding a bright red solution with alcohol or acetic acid. The crystals absorb CO_2 from the air, and become red. Rosaniline is a triamine, and forms monacid, di-acid, and tri-acid salts. The monacid salts yield red solutions, changed to brown by excess of acid from formation of tri-acid salts, which are decomposed again by water. The red solutions are bleached by zinc and sulphuric acid, or by ammonium sulphide, the rosaniline being converted into *leucaniline*, $C_{20}H_{21}N_3$, which gives colourless tri-acid salts. Oxidising agents reproduce the red colour. Commercial aniline also yields rosaniline hydrochloride when heated with chlorinating agents, such as stannic and mercuric chlorides. A fragment of corrosive sublimate fused in a test-tube with a little aniline quickly converts part of it into rosaniline hydrochloride.* When rosaniline acetate is boiled with excess of aniline, the rosaniline becomes *triphenyl-rosaniline*, ammonia being evolved—

$$C_{20}H_{19}N_3 + 3(NH_2.C_6H_5) = C_{20}H_{16}(C_6H_5)_3N_3 + 3NH_3.$$

On treating with hydrochloric acid, *triphenylrosaniline hydrochloride*, or *aniline blue*, or *opal blue*, is obtained; it is insoluble in water, but crystallises from hot alcohol. By dissolving it in alcoholic ammonia, and adding water, a white precipitate of $C_{20}H_{16}(C_6H_5)_3N_3.H_2O$, is obtained, which becomes blue in the air, and yields blue salts with acids. By heating rosaniline acetate with two molecules of aniline, a violet dye is obtained which contains *diphenyl-rosaniline*. If aniline blue be heated with fuming sulphuric acid, it is converted into *triphenyl-rosaniline monosulphonic acid*, $C_{20}H_{16}(C_6H_5)_2C_6H_4(HSO_3)N_3$, which is precipitated by water, and dissolved in soda, to form the sodium-salt used as *alkali blue*, or *Nicholson's blue*. *Soluble blue* is the *sodium triphenyl-rosaniline disulphonate*. By the action of methyl iodide in closed vessels, a violet dye containing *trimethyl-rosaniline methyliodide*, $C_{20}H_{16}(CH_3)_3N_3.CH_3I$, is obtained. *Iodine green* contains an additional CH_3I; both are formed when rosaniline acetate is heated, in a closed vessel, to 100°, for some hours, with methyl alcohol and excess of methyl iodide; after distilling off the excess, the iodine green is extracted from the residue by a strong solution of NaCl. It forms splendid green crystals soluble in alcohol. The commercial iodine green is usually the picrate. It retains its green colour by candle-light. Ethyl and amyl iodides yield similar colours. *Aldehyd green* is prepared by the action of aldehyd on rosaniline dissolved in sulphuric acid at 100°, the blue solution being poured into a boiling solution of sodium thiosulphate; on boiling, the green is formed, and may be precipitated from the solution by sodium acetate; its constitution is not known.

Chrysaniline, $C_{20}H_{17}N_3$, is found among the secondary products in the preparation of aniline red. It is a bright yellow powder, nearly insoluble in water, but soluble in alcohol. Diluted hydrochloric acid dissolves it, and, on adding the strong acid, a scarlet crystalline precipitate of $C_{20}H_{17}N_3.2HCl$ is obtained. The sparing solubility of its nitrate is remarkable; even from a weak solution of the hydrochloride, nitric acid precipitates $C_{20}H_{17}N_3.HNO_3$ in red needles. Chrysaniline forms monacid and di-acid salts.

Malachite green, $C_{23}H_{26}N_2$, is obtained by heating benzoic aldehyd with dimethylaniline and zinc chloride; $C_6H_5.COH + 2N(CH_3)_2C_6H_5 = C_{23}H_{26}N_2 + H_2O$; it forms green crystals; the zinc chloride acts as a dehydrating agent.

463. *Xylidine*, $NH_2.C_8H_9$, or *amido-xylene*, $C_6H_3(CH_3)_2.NH_2$, is isomeric with dimethylaniline, and may be prepared by the reduction of nitro-xylene. There are three isomeric xylidines, distinguished as ortho-, meta-, and para-xylidine; they are all liquid. Xylidine, like toluidine, forms colouring matters with aniline under the influence of oxidising or

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* Rosaniline is also produced by oxidising toluidine with nitrobenzene—

$$2NH_2C_7H_7 + C_6H_5NO_2 = C_{20}H_{19}N_3 + 2H_2O.$$

chlorinising agents; *xylidine-rosaniline* forms crimson salts, and is produced by the reaction $NH_2.C_6H_5 + 2(NH_2.C_8H_9) = C_{22}H_{23}N_3 + H_6$.

Cymidine, $NH_2.C_{10}H_{13}$, or *amido-cymene*, $C_6H(CH_3)_4.NH_2$, is obtained by the reduction of nitro-cymene.

Benzylamine, $C_6H_5.CH_2.NH_2$, is produced by the action of benzyl chloride upon ammonia in alcoholic solution: $C_6H_5.CH_2Cl + NH_3 = C_6H_5.CH_2.NH_2.HCl$. By distilling the hydrochloride with potash, it is obtained as a colourless liquid, boiling at 183°. It is metameric with toluidine, and differs greatly from it, being easily soluble in water, and strongly alkaline. It is a more powerful base than toluidine.

Dibenzylamine, $(C_6H_5.CH_2)_2NH$, and *tribenzylamine*, $(C_6H_5.CH_2)_3N$, are formed in the same reaction as benzylamine. The secondary amine is a liquid, boiling at about 300° C., and the tertiary is a crystalline body, soluble in hot alcohol.

Naphthylamine, or *naphthalidine*, $NH_2.C_{10}H_7$, or *amido-naphthalene*, is prepared from nitro-naphthalene, $C_{10}H_7.NO_2$, in the same way as aniline from nitrobenzene. It forms colourless needles, having a disagreeable smell of mice, fusing at 50° C. and boiling at 300° C. It dissolves sparingly in water, but easily in alcohol, and forms well-crystallised salts, which give, with ferric chloride, a blue precipitate, changing to purple *oxynaphthylamine*, $C_{10}H_9NO$. An isomeric, or *β-naphthylamine*, is known, which gives no colour with ferric chloride.

Diamido-naphthalene, $(NH_2)_2.C_{10}H_6$, or *naphthylene diamine*, $N_2H_4(C_{10}H_6)''$, corresponding to phenylene diamine, is obtained by the reduction of dinitronaphthalene; it is a crystalline base. There are two other bases isomeric with it.

Diazo-naphthalene nitrate, $C_{10}H_7N_2.NO_3$, corresponding to diazobenzene nitrate, is an unstable salt formed by the action of nitrous acid on naphthylamine nitrate; $C_{10}H_7.NH_3.NO_3 + HNO_2 = C_{10}H_7N.N.NO_3 + 2H_2O$. This, when boiled with water, decomposes like diazobenzene nitrate, yielding naphthol, $C_{10}H_7.OH$, in place of phenol; $C_{10}H_7N_2.NO_3 + H_2O = C_{10}H_7.OH + N_2 + HNO_3$.

Amido-azo-naphthalene, $C_{10}H_7.N.N.C_{10}H_6.NH_2$, is prepared, like the benzene derivative, by adding an alkaline nitrite to a solution of naphthylamine in HCl. It crystallises from alcohol in red needles with a green metallic lustre, and yields violet salts which are di-acid.

Magdala red, or *naphthalene red*, $C_{30}H_{21}N_3.HCl.Aq$, is the hydrochloride of a base similar to rosaniline, obtained by heating amidoazonaphthalene with naphthylamine: $C_{20}H_{15}N_3 + C_{10}H_9N = C_{30}H_{21}N_3 + NH_3$. The hydrochloride crystallises in needles with a green lustre, yielding a red highly fluorescent solution in alcohol.

Diazo-amido-naphthalene, $C_{10}H_7.N_2.NHC_{10}H_7$, is metameric with amidoazonaphthalene, and is obtained by passing N_2O_3 into a cold solution of naphthylamine; $2(C_{10}H_7.NH_2) + HNO_2 = C_{10}H_7.N_2.NHC_{10}H_7 + 2H_2O$. It forms brown crystals, which are explosive, and are decomposed when heated with acids, yielding naphthylamine and naphthol: $C_{10}H_7.N_2.NHC_{10}H_7 + H_2O = NH_2.C_{10}H_7 + C_{10}H_7.OH + N_2$.

464. AMIDES.—The amides may be regarded as composed upon the model of NH_3, by the substitution of a negative or acid radical for hydrogen; thus, acetamide, $NH_2.C_2H_3O$, has the radical acetyl, C_2H_3O, replacing one-third of the H in NH_3. The amides, like the amines (p. 574), may be primary, secondary, or tertiary accordingly as one, two, or three atoms of H in the NH_3 group has been replaced, and they may be monamides, diamides, or triamides, accordingly as they are formed upon the model of one, two, or three ammonia molecules.

Amides may be formed from ammonia, in the same manner as amines, by the action of the chloride of a negative radical, when the chlorine removes the ammonia-hydrogen, or by the action of an ethereal salt, when the hydrogen is exchanged for the acid radical. Amides may also be formed from the acids by combining them with ammonia, and dehydrating by heat or otherwise, when the ammonia-hydrogen and the HO group of the acid will form water, leaving the NH_2 group in combination with the acid radical. This mode of formation explains the characteristic property of the amides to be converted by hydrolysis (or assimilation of the elements of water) into ammonia-salts.

Formamide, $NH_2.HCO$, may be obtained by distilling ammonium formate; $NH_4.CO.OH = NH_2.HCO + HOH$; or by saturating ethyl formate with ammonia and heating to 100°, for two days, in a sealed tube—

$$HCO.OC_2H_5 + NH_3 = HCO.NH_2 + HO.C_2H_5.$$

It is a liquid, boiling at 195° C., part of it being decomposed, yielding water, carbonic oxide, ammonia, and hydrocyanic acid—

$$2(NH_2.HCO) = H_2O + CO + NH_3 + HCN.$$

Strong potash converts it, at once, into potassium formate and ammonia—

$$NH_2.HCO + KHO = HCO.OK + NH_3.$$

Formamide is also produced by the distillation of ammonium oxalate.

Methyl formamide, $NH.CH_3.CHO$, is obtained by distilling methylamine formate.

Ethyl formamide is produced by the action of ethylamine on ethyl formate.

Ethylene diformamide, $N_2H_2(C_2H_4)''(CHO)_2$, is formed when ethylene-diamine is heated with chloral; $N_2H_4(C_2H_4)'' + 2CCl_3CHO = N_2H_2(C_2H_4)''(CHO)_2 + 2CHCl_3$. It is a liquid, which is decomposed, when heated with acids or alkalies, into ethylene-diamine and formic acid.

Acetamide, $NH_2.CH_3.CO$, is prepared by decomposing ethyl acetate with strong ammonia; $CH_3.CO.OC_2H_5 + NH_3 = CH_3.CO.NH_2 + HO.C_2H_5$; the reaction takes place even in the cold, but more rapidly on heating; on distilling the product, that which distils above 200° C. is chiefly acetamide. It may also be obtained by distilling ammonium acetate; $CH_3.CO.ONH_4 = CH_3.CO.NH_2 + H_2O$; or by distilling a mixture of ammonium chloride with dry sodium acetate. The reaction between ammonia and acetyl chloride also yields acetamide—

$$2NH_3 + C_2H_3O.Cl = NH_2.C_2H_3O + NH_4Cl.$$

It crystallises in needles smelling of mice, fusing at 78° C. and boiling at 222° C., soluble in water and alcohol, but sparingly in ether. It acts as a weak base, forming unstable crystalline salts. Solution of acetamide dissolves silver oxide, and deposits *silver acetamide*, $C_2H_3O.NHAg$. With mercuric oxide, crystals of *mercuric acetamide*, $(C_2H_3O.NH)_2Hg$, are obtained. Boiling with water, especially in presence of acids or alkalies, converts acetamide into acetic acid and ammonia; $NH_2.C_2H_3O + HOH = NH_3 + HO.C_2H_3O$. When distilled with powerful dehydrating agents, such as P_2O_5 or $ZnCl_2$, it yields *acetonitrile*, or *methyl cyanide*—

$$NH_2.C_2H_3O = NC.CH_3 + H_2O.$$

The three chloracetic acids yield corresponding amides—*monochloracetamide*, $NH_2.C_2H_2ClO$; *dichloracetamide*, $NH_2.C_2HCl_2O$; and *trichloracetamide*, $NH_2.C_2Cl_3O$, all crystalline solids with high boiling points.

Ethyl acetamide, $NH.C_2H_5.C_2H_3O$, is a liquid formed when ethylamine acts on ethyl acetate.

Di-acetamide, $NH(C_2H_3O)_2$, is obtained by heating acetamide in hydrochloric acid gas; $2NH_2.C_2H_3O + HCl = NH(C_2H_3O)_2 + NH_4Cl$; or by acting on acetamide with acetyl chloride; $NH_2.C_2H_3O + C_2H_3O.Cl = NH(C_2H_3O)_2 + HCl$. It forms crystals soluble in water, and having weak acid properties.

Tri-acetamide, $N(C_2H_3O)_3$, is obtained by heating acetonitrile with acetic anhydride to 200° C.; $NC.CH_3 + (C_2H_3O)_2O = N(C_2H_3O)_3$. It may be crystallised from ether, and is neither basic nor acid.

Propionamide, $NH_2.C_3H_5O$, and *butyramide*, $NH_2.C_4H_7O$, are prepared like acetamide.

Valeramide, $NH_2.C_5H_9O$, is obtained by heating valeric acid with ammonium thiocyanate; $C_5H_9O.OH + NH_4S.CN = NH_2.C_5H_9O + NH_3 + SCO$.

The amides of the higher fatty acids, palmitic, stearic, and oleic, are formed when their glycerine ethereal salts, palmitine, stearine, and oleine, are treated with strong ammonia.

Benzamide, $NH_2.C_7H_5O$, is precipitated when benzoyl chloride is treated with ammonia; $C_7H_5O.Cl + 2NH_3 = NH_2.C_7H_5O + NH_4Cl$. It may be crystallised from hot water in plates, which fuse at 125° C., and sublime at 290° C. It is soluble in alcohol and ether, and resembles acetamide in its reactions; it forms a crystalline compound with HCl, and its aqueous solution dissolves mercuric oxide, *benzomercuramide*, $NHg.C_7H_5O$, being produced. Benzamide is converted into benzoic acid and ammonia when boiled with acids or alkalies—

$$NH_2.C_7H_5O + HOH = HO.C_7H_5O + NH_3.$$

Heated with benzoic anhydride, it yields benzoic acid and benzonitrile—

$$(C_7H_5O)_2O + NH_2.C_7H_5O = 2(HO.C_7H_5O) + NC.C_7H_5.$$

With benzoyl chloride, the same products are formed—

$$C_7H_5O.Cl + NH_2.C_7H_5O = HO.C_7H_5O + NC.C_7H_5 + HCl.$$

Benzamide is produced when hippuric acid is boiled with lead peroxide—

$$C_8H_8NO.CO_2H + 3PbO_2 = NH_2.C_7H_5O + 2CO_2 + H_2O + 3PbO.$$

Glycolamide, $NH_2.C_2H_3O_2$, is obtained by acting upon ethyl glycolate with ammonia; $C_2H_3O_2.OC_2H_5 + NH_3 = C_2H_3O_2.NH_2 + HO.C_2H_5$. It crystallises in needles, soluble in water, and easily converted by alkalies and acids into ammonia and glycolic acid. Glycolamide is also formed by heating *glycolide* in ammonia gas; glycolide being an amorphous insoluble product of the action of heat upon glycolic acid—

$$2(CH_2.HO.CO.OH)\ (\textit{glycolic acid}) = (CH_2.CO)_2O_2\ (\textit{glycolide}) + 2H_2O;$$

$$2NH_3 + (CH_2.CO)_2O_2 = 2(NH_2.CO.CH_2.OH)\ (\textit{glycolamide}).$$

Glycolamide is metameric with glycocine (amidoacetic acid).

Lactamide, $NH_2.C_3H_5O_2$, results from the action of ammonia upon ethyl lactate or upon lactide (p. 523), which bears the same relation to lactic acid as glycolide bears to glycolic acid—

$$2(CHCH_3.HO.CO.OH)\ (\text{lactic acid}) = (CHCH_3.CO)_2O_2\ (\text{lactide}) + 2H_2O;$$

$$2NH_3 + (CHCH_3CO)_2O_2 = 2(NH_2.CO.CHCH_3.OH)\ (\text{lactamide}).$$

Lactamide forms crystals which may be fused and volatilised without decomposition; it is soluble in water and alcohol. It yields ammonia and lactic acid when boiled with acids or alkalies.

465. The formation of the amides of the acids of the lactic series from the compounds corresponding to glycolide and lactide helps to explain the constitution of these acids, which are often spoken of as *di-atomic* or *dihydric monobasic acids*, or *alcohol acids* (p. 524), since they contain two HO groups, one of which behaves in the same way as the HO in alcohols, and the other forms part of the CO.OH group of the monobasic acids. Thus, the action of heat upon these acids produces two anhydrides, by the successive loss of two hydroxyl groups in the form of water. One molecule of the acid plays the part of an acid molecule towards another which acts as an alcohol molecule, forming *ethereal derivatives* by separation of H_2O, just as ordinary alcohols and acids form ethereal salts; for example—

$$\underbrace{CH_2.HO.CO.OH}_{\text{Glycolic } \textit{acid} \text{ molecule.}} + \underbrace{CH_2.CO.(OH)_2}_{\text{Glycolic } \textit{alcohol} \text{ molecule.}} = HOH + \underbrace{(CH_2.CO.OH).O.(CH_2.CO.OH).}_{\textit{First ethereal anhydride.}}$$

Again—

$$CH_2.HO.CO.OH + CH_2.CO(OH)_2 = 2HOH + \underbrace{(CH_2.CO).O_2.(CH_2.CO).}_{\textit{Second ethereal derivative}\text{, or Glycolide.}}$$

When an amide is produced by the action of ammonia upon a true anhydride, water is always produced, but when ammonia acts upon glycolide or lactide, there is no separation of water, because the HO has been already eliminated.

466. *Oxamide*, $N_2H_4.C_2O_2$, is a primary di-amide, which is best prepared by shaking ethyl oxalate with solution of ammonia, when the mixture becomes hot and a white crystalline precipitate of oxamide separates; $C_2O_2(OC_2H_5)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2(HO.C_2H_5)$. If an alcoholic solution of ammonia be employed, or if ammonia gas be passed into ethyl oxalate, only half the ethoxyl (OC_2H_5) is replaced by NH_2, and a crystalline body soluble in water is obtained; this is *oxamethane*, $C_2O_2.OC_2H_5.NH_2$. Oxamide is scarcely dissolved by water, alcohol, or ether, and is a perfectly neutral body. It may be crystallised in needles from a hot saturated solution of calcium chloride. When heated, a part sublimes unchanged. A red-hot tube decomposes the vapour, forming hydrocyanic acid and urea, $2N_2H_4C_2O_2 = HCN + N_2H_4CO + CO + CO_2 + NH_3$. When boiled with acids, oxamide yields oxalic acid and ammonium salts; $(NH_2)_2C_2O_2 + H_2SO_4 + 2H_2O = (HO)_2C_2O_2 + (NH_4)_2SO_4$. Boiled with alkalies, it yield oxalates and ammonia; $(NH_2)_2C_2O_2 + 2KOH = (KO)_2C_2O_2 + 2NH_3$.

Oxamide is obtained by the distillation of ammonium oxalate; $C_2O_2(ONH_4)_2 = C_2O_2(NH_2)_2 + 2H_2O$, showing that the ammonium salt of a dibasic acid yields a di-amide. Since it contains the elements of cyanogen, it is not surprising to meet with oxamide in many reactions of cyanogen compounds; it can be formed by mixing aqueous solutions of hydrocyanic acid and hydric peroxide; $2HCN + H_2O_2 = 2NH_2.C_2O_2$. The reaction of aldehyd with solution of cyanogen also produces oxamide; and it is found among the products of the action of nitric acid on potassium ferrocyanide. The oxidation of potassium cyanide with manganese dioxide and dilute sulphuric acid also forms oxamide.

Dimethyl oxamide, $N_2H_2(CH_3)_2.C_2O_2$, and *di-ethyl oxamide*, $N_2H_2(C_2H_5)_2.C_2O_2$, are formed by the action of methylamine and ethylamine on ethyl oxalate. They crystallise from hot water.

By acting on di-ethyl oxamide with PCl_5, a remarkable tertiary amine has been obtained, called *chloroxalethyline*, and having the formula $C_6H_9ClN_2$; it is an alkaline liquid, which boils at 217° C., and when acted on by hydriodic acid and red phosphorus, it yields, on distillation with soda, another liquid base, *oxalethyline*, $C_6H_{10}N_2$, which is poisonous, and produces the same symptoms as atropine, notably the dilatation of the pupil of the eye.

467. The study of the amides of dibasic acids shows that amides may often be conveniently regarded as derived from acids by the substitution of the NH_2 group for the OH group. Thus, benzoic acid, $C_6H_5.CO.OH$, yields benzamide, $C_6H_5.CO.NH_2$; lactic acid, $C_2H_5O.CO.OH$, yields lactamide, $C_2H_5O.CO.NH_2$; oxalic acid, $C_2O_2(OH)_2$, yields oxamide, $C_2O_2(NH_2)_2$. This makes it evident that a dibasic acid may form two amides; thus, oxalic acid yields $C_2O_2.OH.NH_2$, *oxamic acid*, in which half the hydroxyl is replaced by amidogen.

Oxamic acid, $CO.NH_2.CO.OH$, is prepared by heating hydro-ammonium oxalate (acid oxalate) till it begins to give off CO_2—

$$C_2O_2.OH.ONH_4 = CO.NH_2.CO.OH + H_2O.$$

A mixture of oxamide and oxamic acid is left, from which water extracts the acid. Ammonium oxamate is formed when oxamide is boiled with solution of ammonia; $C_2O_2(NH_2)_2 + H_2O = CO.NH_2.CO.ONH_4$. On adding HCl, the oxamic acid is obtained as a crystalline precipitate, sparingly soluble in water, alcohol, and ether, and converted into hydro-ammonium oxalate by boiling with water. It fuses at 173°, and decomposes, yielding oxamide, formic acid, and water.

Ethyl oxamate, $CO.NH_2.CO.OC_2H_5$, is identical with oxamethane. It crystallises in needles, easily soluble in water and alcohol, and distilling undecomposed.

Succinamide, $N_2H_4.C_4H_4O_2$, is produced by the action of ammonia on ethyl succinate. It crystallises in needles, which are sparingly soluble in cold water, alcohol, and ether. When heated to 200° C., it yields ammonia and *succinimide*; $C_2H_4(CO)_2(NH_2)_2 = NH_3 + C_2H_4(CO)_2NH$. This body is also formed when ammonium succinate is distilled. It is crystalline, and soluble in water and alcohol. By mixing the hot alcoholic solution with a little ammonia and silver nitrate, *silver succinimide*, $C_2H_4(CO)_2NAg$, is obtained in crystals.

The *imides*, which contain the group NH (imidogen), exhibit an acid character, allowing the H of this group to be replaced by a metal.

468. *Succinamic acid*, $C_2H_4(CO.NH_2)(CO.OH)$, is prepared from the barium salt obtained by heating succinimide with solution of barium hydrate—

$$2C_2H_4(CO)_2NH + Ba(HO)_2 = (C_2H_4.CO.NH_2.CO.O)_2Ba.$$

The barium succinamate is decomposed by sulphuric acid—

$$(C_2H_4.CO.NH_2.CO.O)_2Ba + H_2SO_4 = 2(C_2H_4.CO.NH_2.CO.OH) + BaSO_4.$$

The filtrate from the barium sulphate deposits crystals of succinamic acid.

Amido-succinamic acid, $C_2H_3.NH_2(CO.NH_2)(CO.OH)$, or *asparagine*, is found in the shoots of asparagus and of other plants grown in the dark. It is of very frequent occurrence in plants, being found in marsh-mallow, vetches, peas, beans, mangold-wurzel, lettuces, potatoes, chestnuts, and dahlia roots. It may be extracted from the expressed juices of the plants by boiling to coagulate the albumen, filtering, and evaporating to a syrup, when the asparagine crystallises, on standing, in rhombic prisms containing H_2O, which may be recrystallised from boiling water. It is nearly insoluble in alcohol and ether. Like many bodies containing the NH_2 group, it is capable of acting as a weak acid and a weak base. In contact with ferments, asparagine is converted into ammonium succinate. When acted on by nitrous acid, asparagine is converted into malic acid—

$$C_2H_3.NH_2(CO.NH_2)(CO.OH) + 2HNO_2 = C_2H_3.OH(CO.OH)(CO.OH) + N_4 + 2H_2O.$$

From this reaction it was formerly inferred that asparagine was the amide of malic acid, with which, however, it is only isomeric. Ordinary asparagine is lævorotatory (p. 536), but an isomeride has been found in the mother-liquor from crude asparagine, which is dextrorotatory to the same extent, and is much sweeter than ordinary asparagine. A solution of the two in equal proportions is inactive, but the asparagines are deposited from it in crystals, which are, respectively, right- and left-handed. The isomeric derivatives from each kind retain the optical properties of their source. When asparagine is boiled with acids or alkalies, it is converted into *amidosuccinic* or *aspartic acid*—

$$C_2H_3.NH_2.(CO.NH_2)(CO.OH) + H_2O = C_2H_3.NH_2.(CO.OH)(CO.OH) + NH_3.$$

Aspartic acid is sparingly soluble in cold water and alcohol, but may be crystallised from hot water. Nitrous acid substitutes OH for the NH_2 in aspartic acid, converting it into malic acid. Aspartic acid is found in the molasses from beet-root juice, and occurs among the products of the action of sulphuric acid and of zinc chloride upon albuminous substances.

Malamide, $N_2H_4.C_4H_4O_3$, is obtained by acting with alcoholic ammonia upon ethyl malate; it crystallises from an aqueous solution, but the crystals, unlike those of asparagine, are anhydrous. When boiled with acids or alkalies, it yields ammonia and malic (instead of aspartic) acid—

$$C_2H_3.OH.(CO.NH_2)_2 + 2H_2O = 2NH_3 + C_2H_3.OH(CO.OH)_2.$$

469. *Carbamide*, or *urea*, $N_2H_4.CO$, or *carboxyl-diamine*, is the diamide of carbonic acid $(HO)_2CO$, and is produced when ammonia acts upon ethyl carbonate at 180° C.—

$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2HOC_2H_5;$$

also when ammonia acts on carboxyl chloride (phosgene)—

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

Oxamide may be converted into urea by heating it with mercuric oxide; $C_2O_2(NH_2)_2 + HgO = CO(NH_2)_2 + Hg + CO_2$. But the best process for preparing it is to heat a solution of ammonium isocyanate, $NH_4.NCO$, which is metameric with urea; this method will be described under cyanogen derivatives.

Urea is the chief form in which the nitrogen of the effete tissues is excreted from the human organism, and it is present in urine to the amount of about 1.4 per cent. by weight. To extract it, the urine is filtered to separate mucus, evaporated to about an eighth of its bulk, cooled, and mixed with about an equal volume of strong nitric acid, which must be quite colourless, showing it to be free from nitrous acid, which would decompose the urea; the latter is precipitated in pearly scales of urea nitrate, which is nearly insoluble in nitric acid, and sparingly soluble in water. This is collected on a filter, washed with ice-cold water till the washings are but slightly coloured, dissolved in boiling water, and mixed with precipitated barium carbonate rubbed to a cream with water, as long as a fresh addition of the carbonate causes effervescence—

$$2(N_2H_4CO.HNO_3) + BaCO_3 = CO_2 + 2N_2H_4CO + H_2O + Ba(NO_3)_2.$$

After filtering from the excess of $BaCO_3$, the liquid is evaporated on a steam-bath, when a mixture of urea and barium nitrate is obtained, from which the urea may be extracted by strong alcohol, and crystallised by evaporation. It crystallises in long prisms resembling nitre, which dissolve in an equal weight of cold water, and in five parts of cold alcohol; urea is almost insoluble in ether. When heated, urea fuses at 130° C., and evolves much ammonia and some ammonium cyanate. If kept for some time at 150° C., the bulk of it is converted into *biuret*, or *dicarbonyl-diamid-imide*, produced from two molecules of urea by the loss of one molecule of ammonia—

$$2CO(NH_2)_2 = NH_3 + (CO)_2(NH_2)_2NH.$$

When the temperature is raised to 170° C., the biuret again evolves ammonia, and is converted into cyanuric acid—

$$3(CO)_2(NH_2)_2NH = 3NH_3 + 2(CN)_3(HO)_3.$$

Urea is not alkaline, but, like many amides, it is a weak base, and though a di-amide, forms salts like a monacid base; these are acid to litmus; the nitrate and oxalate are best known because they are sparingly soluble, and are obtained as crystalline precipitates when nitric and oxalic acids are stirred with solution of urea. The nitrate, when heated, evolves a very pungent smell, and is decomposed, with almost explosive violence, at 150° C. *Urea oxalate* crystallises with 2Aq; $(N_2H_4CO)_2.H_2C_2O_4.2Aq$. *Urea hydrochloride*, $N_2H_4CO.HCl$, is formed, with evolution of heat, when HCl gas acts on dry urea; it solidifies to a crystalline deliquescent mass, which is decomposed by water.

Urea, like many other amides, forms compounds with the oxides of silver and mercury. The compound $N_2H_4CO.3Ag_2O$ is obtained as a grey crystalline powder when silver oxide is digested in solution of urea. When mercuric oxide is treated in the same way, the compound $N_2H_4CO.HgO$ is formed; on adding mercuric chloride to a solution of urea mixed with potash, a white precipitate of $2N_2H_4CO.3HgO$ is obtained, but if mercuric nitrate be employed, the precipitate is $N_2H_4CO.2HgO$. The formation of the last compound is the basis of Liebig's method for the determination of urea.

Urea also forms compounds with certain salts; the compound $N_2H_4CO.NaCl.Aq$ is obtained in crystals when urine is evaporated to a small bulk. When strong solutions of urea and $AgNO_3$ are mixed, crystals of $N_2H_4CO.AgNO_3$ are deposited. By mixing dilute solutions of urea and mercuric nitrate, a precipitate is formed having the formula $N_2H_4CO(HgO)_2HNO_3$.

Urea, being the di-amide of carbonic acid, would be expected to yield ammonia and carbonic acid when boiled with acids or alkalies. On boiling solution of urea with potash, $(NH_2)_2CO + 2KOH = 2NH_3 + (KO)_2CO$; but the action is slow in weak solutions.

When urea is heated with strong sulphuric acid, $(NH_2)_2CO + H_2O + 2H_2SO_4 = CO_2 + 2NH_4HSO_4$. Even on boiling solution of urea in water, it is slowly converted into ammonium carbonate, and the change takes place quickly when urea is heated with a little water to 230° C., in a sealed tube; $(NH_2)_2CO + 2H_2O = (NH_4)_2CO_3$. Urea undergoes the same transformation into ammonium carbonate when urine is allowed to putrefy.

Nitrous acid acts upon urea, as upon the amides generally, converting the NH_2 into OH, and liberating N, but the $(HO)_2CO$ which is formed is at once decomposed into H_2O and CO_2: $(NH_2)_2CO + 2HNO_2 = N_4 + CO_2 + 3H_2O$. Hypochlorites and hypobromites (prepared by dissolving bromine in alkalies) also expel all the nitrogen as gas—

$$(NH_2)_2CO + 3NaOBr + 2NaOH = N_2 + 3H_2O + Na_2CO_3 + 3NaBr.$$

This method is sometimes adopted for determining urea by measuring the nitrogen gas. The nitrogen is also liberated when urea is boiled with potash and a large excess of potassium permanganate, whereas, in most other amides, the bulk of the nitrogen is oxidised to nitric acid. When chlorine is passed into fused urea, hydrochloric acid and nitrogen are evolved, and the residue is a mixture of cyanuric acid with ammonium chloride—

$$3N_2H_4CO + Cl_3 = HCl + N + (CN)_3(HO)_3 + 2NH_4Cl.$$

By boiling solution of urea with $AgNO_3$, a crystalline precipitate of silver isocyanate is obtained; $N_2H_4CO + AgNO_3 = NH_4NO_3 + AgNCO$.

Urea has been formed by passing NH_3 and CO_2, together through a red-hot tube; and by passing a mixture of benzene-vapour, ammonia, and air over red-hot platinum wire.

Biuret, or *allophanamide*, $(CO)_2(NH_2)_2NH$, is obtained by heating urea to 150° C.

as long as it evolves ammonia freely, extracting the residue with cold water, which leaves most of the cyanuric acid undissolved, precipitating the rest by lead acetate, removing the lead by H_2S, and evaporating the filtered solution, when the biuret crystallises with one molecule of water. It is soluble in alcohol. Its aqueous solution, rendered alkaline by potash, gives a fine violet colour with cupric sulphate. When heated in HCl gas, biuret is converted into guanidine hydrochloride; $(CO)_2(NH_2)_2NH + HCl = CO_2 + C(NH_2)_2NH.HCl$.

470. *Carbamic acid*, $CO.NH_2OH$, has not been obtained in the free state, but *ammonium carbamate* is formed when ammonia combines with carbonic acid gas; $2NH_3 + CO_2 = CO.NH_2.ONH_4$. The ammonium salt is best prepared by saturating absolute alcohol with dry ammonia gas, and passing dry CO_2 into the solution, when the ammonium carbamate crystallises out. It is soluble in water, and is converted into ammonium carbonate by boiling the solution; $CO.NH_2.ONH_4 + H_2O = CO(ONH_4)_2$. Ammonium carbamate sublimes below 100° C., and when heated, in a sealed tube, to 135° C., yields urea and ammonium carbonate—

$$2(CO.NH_2.ONH_4) = CO(NH_2)_2 + CO(ONH_4)_2.$$

When ammonium carbonate is distilled, part of it is converted into the carbamate; $CO(ONH_4)_2 = CO.NH_2(ONH_4) + H_2O$. This accounts for the presence of ammonium carbamate in the commercial carbonate (p. 270).

Ethyl carbamate, or *urethane*, $CO.NH_2.OC_2H_5$, is formed by the action of solution of ammonia upon ethyl carbonate at 100° C.—

$$CO(OC_2H_5)_2 + NH_3 = CO.NH_2.OC_2H_5 + HO.C_2H_5.$$

It forms tabular crystals, soluble in water, alcohol, and ether, distilling without decomposition. Boiled with potash, it yields the carbonate, alcohol, and ammonia; $CO.NH_2.OC_2H_5 + 2KOH = CO(OK)_2 + NH_3 + HO.C_2H_5$. Heated with ammonia, it gives alcohol and urea; $CO.NH_2.OC_2H_5 + NH_3 = CO(NH_2)_2 + HO.C_2H_5$. The carbamates of methyl, propyl, &c., have been obtained.

Ethyl allophanate, $CO.NH_2.NH.CO.OC_2H_5$, is formed when urea is acted on by ethyl chlorocarbonate (prepared by saturating alcohol with carbonyl chloride); $CO(NH_2)_2 + COCl.OC_2H_5 = CO.NH_2.NH.CO.OC_2H_5 + HCl$. It crystallises in prisms soluble in water and alcohol. Allophanic acid has not been obtained; when liberated from its salts, it decomposes into CO_2 and urea; $CO.NH_2.NH.CO.OH = CO(NH_2)_2 + CO_2$. When heated with alcoholic ammonia, in a sealed tube, to 100° C., ethyl allophanate is converted into biuret, which is the amide of allophanic acid; $CO.NH_2.NH.CO.OC_2H_5 + NH_3 = CO.NH_2.NH.CO.NH_2 + HO.C_2H_5$.

The hydrogen in urea, like that in ammonia, admits of replacement by positive or negative radicals, forming so-called *compound ureas*. Those containing positive radicals, such as *methyl carbamide*, $CO.NH_2.NHCH_3$, and *dimethyl carbamide*, $CO(NHCH_3)_2$, are derived from the cyanogen compounds, and will be noticed under that head. *Acetyl carbamide*, or *acetyl urea*, $CO.NH_2.NHC_2H_3O$, is a crystalline substance obtained by the action of acetyl chloride upon urea; it is not basic. *Di-acetyl carbamide* is formed when acetamide is heated to 50° C. with carbonyl chloride; $2NH_2C_2H_3O + COCl_2 = CO(NHC_2H_3O)_2 + 2HCl$. The compound ureas which contain acid radicals in place of hydrogen are also called *ureides*.

Sulphurea will be noticed under cyanogen compounds.

Sulphocarbamic acid, $CS.NH_2.SH$, is obtained as an ammonium salt by acting on carbon disulphide with ammonia in alcoholic solution; $2NH_3 + CS_2 = CS.NH_2.SNH_4$, the reaction corresponding to that between NH_3 and CO_2. The ammonium sulphocarbamate crystallises in yellow prisms. When decomposed by HCl, it yields sulphocarbamic acid as a yellow unstable crystalline body, which decomposes spontaneously; $CS.NH_2.SH = H_2S + HSCN$ (sulphocyanic acid).

471. *Anilides* are derived from aniline, $NH_2.C_6H_5$, in the same manner as amides from ammonia, by the replacement of the hydrogen in the NH_2 group by an acid radical, and they resemble the amides in their chemical reactions; *formanilide* is $NH.CHO.C_6H_5$; *acetanilide*,

$NH.C_2H_3O.C_6H_5$; *oxanilide*, $N_2H_2(CO)_2(C_6H_5)_2$; *oxanilic* or *phenyl-oxamic* acid, $CO.NH.C_6H_5.CO.OH$.

Carbanilide, or *diphenyl urea*, $(NHC_6H_5)_2CO$, is prepared by heating urea with aniline; $(NH_2)_2CO + 2NH_2C_6H_5 = (NHC_6H_5)_2CO + 2NH_3$. It is slightly soluble in water, more soluble in alcohol, and may be sublimed. Carbanilide is also formed when aniline is acted on by carbonyl chloride.

Thiocarbanilide, or *diphenyl sulphurea*, is formed when aniline is heated with carbon disulphide; $2NH_2C_6H_5 + CS_2 = CS(NHC_6H_5)_2 + H_2S$. It forms colourless crystals, insoluble in water, soluble in alcohol and ether.

472. THE ALKALOIDS, OR VEGETABLE BASES.—These compounds possess particular interest for the chemist, on account of their powerful action on the animal economy, many of them being the active principles of the medicinal or poisonous plants from which they are extracted. Hitherto few of them have been prepared artificially, though the study of their properties indicates that they are ammonia-derivatives. They all contain nitrogen, but rarely more than two atoms in a molecule, though there may be twenty or thirty carbon-atoms. Most of them refuse to sublime without partial decomposition, which unfits them for ranking as *amines;* they dissolve sparingly in water, which renders it unlikely that they are ammonium bases, and brings them nearer to the *amides*, which many of them also resemble in their feebly basic character. The alkaloids are soluble in alcohol, and their solutions are generally alkaline and bitter. Their salts are formed, like those of ammonia, by the direct union of the base and the acid, without separation of water, and, as a rule, the salts are soluble in water. The hydrochlorides of the alkaloids resemble those of all amines, as well as the chlorides of the alkali-metals and the ammonium bases, in forming crystalline double salts with platinic chloride, mercuric chloride, and auric chloride. Most of the alkaloids may be precipitated from their solutions by iodine dissolved in potassium iodide, by potassio-mercuric iodide, by potassio-bismuthic iodide, by picric acid, tannin, metatungstic acid, and phosphomolybdic acid.

473. Three of the natural alkaloids are volatile liquids, and do not contain oxygen; these are coniine, nicotine, and sparteine.

Coniine, $C_8H_{15}N$, is extracted from the seeds of hemlock (*Conium maculatum*) by crushing them and distilling with weak potash. The distillate, which contains ammonia and coniine, is neutralised with sulphuric acid, concentrated by evaporation, and mixed with alcohol to precipitate the ammonium sulphate. On evaporating the filtrate and distilling with strong potash, coniine distils over together with water, upon the surface of which it floats. It is distilled with dried potassium carbonate, to remove water, and the portion distilling at 168° C. is collected separately.

Coniine has a strong odour of mice; its sp. gr. is 0.89, and it boils at 168° C. It is sparingly soluble in cold water, giving an alkaline solution. It dissolves in alcohol and ether. When exposed to air, it becomes brown, and evolves ammonia. Oxidising agents, such as nitric and chromic acids, convert it into butyric acid, $C_4H_8O_2$. With N_2O_3, it gives a yellow liquid, which is decomposed by water into HNO_3 and *azoconydrine*, $C_8H_{14}(NO)N$, which is reconverted into coniine by nascent hydrogen; $C_8H_{14}(NO)N + H_4 = C_8H_{15}N + NH_3 + H_2O$. On distilling azoconydrine with P_2O_5, it yields *conylene*, C_8H_{14}, the sixth homologue of acetylene, a liquid which boils at 126° C., and combines with bromine to form $C_8H_{14}Br_2$. When coniine is heated in a sealed tube with methyl iodide, it exchanges H for CH_3, showing it to be a secondary monamine, $NH(C_8H_{14})''$. The *methyl coniine*, $NCH_3(C_8H_{14})''$, sometimes occurs in hemlock. It combines with methyl iodide to form a crystalline *coniine-methylium iodide*, $N(C_8H_{14})''(CH_3)_2I$, which yields a caustic alkaline hydroxide when decomposed by silver hydroxide. Hemlock also contains another base, *conhydrine*, $C_8H_{17}NO$, crystallising in plates.

Coniine has been obtained artificially by the action of sodium on an alcoholic solution of *allyl pyridine*, $C_5H_4.C_3H_5.N$, a liquid product of the action of paraldehyd upon picoline, C_6H_7N. When coniine hydrochloride is distilled with zinc-dust, it yields *conyrine*, or *propyl-pyridine*, $C_5H_4.C_3H_7N$. If this be heated in a sealed tube with strong hydriodic acid, it is reconverted into coniine.

Paraconiine, $C_8H_{15}N$, isomeric with coniine, is obtained by distilling the product of the action of alcoholic ammonia on butyric aldehyd; $2C_3H_7COH + NH_3 = H_2O + C_8H_{17}NO$ (*dibutyraldine*); $C_8H_{17}NO = H_2O + C_8H_{15}N$ (*paraconiine*). This base is very similar to coniine, and, like it, a powerful narcotic poison, but it has no action on polarised light, whilst coniine is dextrorotatory, and it appears to be a tertiary monamine, for it yields only a methylium iodide when acted on by methyl iodide.

Nicotine, $C_{10}H_{14}N_2$, is found chiefly as malate, in the seeds and leaves of tobacco, *Nicotiana tabacum*, a plant of the order Atropaceæ, many of which, especially deadly nightshade, thorn-apple, henbane, and mandrake, yield narcotic poisons. Nicotine is extracted from tobacco-leaves by digesting them with very dilute sulphuric acid, evaporating to a small bulk, and distilling with excess of potash. The distillate is shaken with ether, which collects the nicotine and rises to the surface; the ethereal layer is drawn off, the ether distilled, and the nicotine placed in contact with quick-lime to remove the water, and distilled in a current of hydrogen, since it is decomposed when distilled in air at the ordinary pressure.

Nicotine is colourless when freshly prepared, but soon becomes brown in air. It smells strongly of tobacco, has sp. gr. 1.048, and boils (in hydrogen) at 180° C. It is soluble in water, alcohol, and ether; its solution is alkaline. It is a di-acid base, but its salts do not crystallise well. When heated with ethyl iodide, it behaves as a tertiary amine, yielding *nicotine-ethylium di-iodide*, $N_2(C_{10}H_{14})''(C_2H_5)_2I_2$, which yields the corresponding caustic alkaline hydroxide when decomposed by silver hydroxide.

By oxidation with chromic acid, nicotine yields *nicotinic acid*, $C_6H_5NO_2$, which yields the base *pyridine*, C_5H_5N, when distilled with lime —

$$Ca(C_6H_4NO_2)_2 + Ca(HO)_2 = 2C_5H_5N + 2CaCO_3.$$

Nicotinic acid has been prepared from malic acid by the following reactions:—When acted on by strong sulphuric acid, malic acid yields water, formic acid, and *coumalinic acid*; $2[C_2H_3.OH.(CO_2H)_2] = 2H_2O + 2HCO_2H + C_5H_3O_2.CO_2H$. Coumalinic acid, acted on by ammonia, yields *hydroxynicotinic acid*; $C_5H_3O_2.CO_2H + NH_3 = H_2O + C_5H_3(OH)N.CO_2H$. This is converted into *chloronicotinic acid*, $C_5H_3ClN.CO_2H$, by phosphoric chloride, and from this, nicotinic acid, $C_5H_4N.CO_2H$, is obtained by the action of tin and hydrochloric acid.

It is worth notice that malic acid (or hydrocalcium malate) exists in tobacco.

Virginian tobacco contains more nicotine than other varieties, the alkaloid amounting to nearly 7 per cent. of the weight of the leaf dried at 212° F., whilst the Maryland and Havannah varieties contain only 2 or 3 per cent. of nicotine. Tobacco is remarkable for the very large amount of ash which it leaves when burnt, amounting to about one-fifth of the weight of the dried leaf, and containing about one-third of potassium carbonate, resulting from the decomposition of the malate, citrate, and nitrate of potassium during the combustion. The presence of this latter salt in large quantity (3 or 4 parts in 100 of the dried leaf) distinguishes tobacco from most other plants, and accounts for the peculiar smouldering combustion of the dried leaves.

Cigars are made directly from the tobacco leaves, which are only moistened with a weak solution of salt in order to impart the requisite suppleness; but *snuff*, after being thus moistened, is subjected, in large heaps, to a fermentation extending over eighteen or twenty months, which results in its becoming alkaline from the development of ammonium carbonate (by the putrefaction of the vegetable albumen in the leaf) and of a minute quantity of free nicotine, which imparts the peculiar pungency to this form of tobacco. The aroma of the snuff appears to be due to the production of a peculiar volatile oil during the fermentation. The proportion of nicotine in snuff is only about 2 per cent., being one-third of that found in the unfermented tobacco; and a great part of this exists in the snuff in combination with acetic acid, which is also a result of the fermentation. It is also not improbable that a little acetic ether is produced, and perhaps some other acids and ethers of the acetic series (*e.g.*, butyric and valerianic), of which extremely minute quantities would give rise to great differences in the aroma of the snuff.

Sparteine, $C_{15}H_{26}N_2$, is a narcotic alkaloid extracted from the common broom (*Spartium scoparium*) by digestion with weak sulphuric acid and decomposing the sulphate by distilling with potash. It is liquid, heavier than water, boiling at 288° C. It is sparingly soluble in water, giving an alkaline solution with a bitter taste. It smells rather like aniline, and becomes brown when exposed to air. It acts as a di-acid base, and appears to be a tertiary di-amine.

474. *Atropine*, or *daturine*, $C_{17}H_{23}NO_3$, is found in deadly nightshade (*Atropa belladonna*) and thorn-apple (*Datura stramonium*), plants of the same order as tobacco. It is obtained by expressing the sap from the flowers of belladonna, heating it to 90° C. to coagulate the albumen, filtering, adding potash to liberate the base, and shaking with chloroform, which collects it and sinks to the bottom. The chloroform is distilled off, and the atropine recrystallised from alcohol. It crystallises in prisms, fusing at 90° C., sparingly soluble in cold water, and having a bitter burning taste and a very poisonous action, with the characteristic effect of dilating the pupil of the eye. Atropine behaves like an amide, for, when boiled with baryta-water or with hydrochloric acid, it yields a crystalline base, *tropine*, $C_8H_{15}NO$, and a crystalline acid, *tropic acid*, $C_8H_9O.CO.OH$—

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_8H_9O.CO.OH.$$

When tropic acid is long boiled with baryta, it yields *atropic* and *isatropic* acids, which are isomeric with cinnamic acid; $C_8H_9O.CO.OH = H_2O + C_8H_7.CO.OH$.

Hyoscyamine, $C_{17}H_{23}NO_3$, is isomeric with atropine, and is associated with it in nightshade and thorn-apple, but it is more abundant in the species of *hyoscyamus* (henbane) belonging to the same order. It is very similar to atropine.

Solanine, $C_{42}H_{87}NO_{16}$, is contained in plants of the order *Solanaceæ*, nearly related to the *Atropaceæ*, especially in *Solanum nigrum* and in the shoots of potatoes (*Solanum tuberosum*) which have been kept in a cellar during winter. To extract it, the plant is digested with weak sulphuric acid, and the solution precipitated with ammonia. It crystallises from alcohol in prisms, which are nearly insoluble in water. It gives a red solution when heated with sulphuric acid and alcohol. When boiled with dilute acids, it yields glucose and *solanidine*, $C_{26}H_{41}NO_2$, a stronger base than solanine.

475. *Opium-alkaloids.*—Opium (ὀπός, *juice*) is obtained from the *Papaver somniferum*, or opium poppy, cultivated in Turkey, Egypt, India, and other Oriental countries. A few days after the poppy-flower has fallen, incisions are made in the poppy-head, when a milky juice exudes. After twenty-four hours, this becomes a soft solid mass of a brown colour, and is scraped off and wrapped in leaves for the market. Opium contains about 25 per cent. of a gummy substance, 20 per cent. of ill-defined organic matters, a little caoutchouc, resin, oil, and water, and variable proportions of a large number of alkaloids, of which morphine, narcotine, and narceine are the most abundant. Some of these have been imperfectly studied, but they are mentioned in the following list—

Hydrocotarnine	$C_{12}H_{15}NO_3$	Papaverine	$C_{21}H_{21}NO_4$
Morphine	$C_{17}H_{19}NO_3$	Meconidine	$C_{21}H_{23}NO_4$
Oxymorphine	$C_{17}H_{19}NO_4$	Laudanosine	$C_{21}H_{27}NO_4$
Codeine	$C_{18}H_{21}NO_3$	Rhæadine*	$C_{21}H_{21}NO_6$
Thebaine	$C_{19}H_{21}NO_3$	Cryptopine	$C_{21}H_{23}NO_5$
Codamine Laudanine	$C_{20}H_{25}NO_4$	Narcotine Lanthopine	$C_{22}H_{23}NO_7$ $C_{23}H_{25}NO_4$
Protopine	$C_{20}H_{19}NO_5$	Narceine	$C_{23}H_{29}NO_9$

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* Found in the field poppy, *Papaver rhœas*.

Morphine, $C_{17}H_{19}NO_3$, is extracted from opium by steeping it in warm water, which dissolves the meconate and sulphate of morphine, straining, and adding calcium chloride, which precipitates calcium meconate. The filtered solution is evaporated to a small bulk and set aside, when the hydrochlorides of morphine, codeine, and oxymorphine crystallise out. These are dissolved in water, and the morphine precipitated by adding ammonia. It is purified by dissolving in alcohol, and crystallising.

Morphine crystallises in prisms, which are almost insoluble in water, requiring 1000 parts of cold and 500 parts of boiling water; it is nearly insoluble in ether and chloroform, both of which dissolve most other alkaloids. It is soluble in ethyl acetate (acetic ether) and in amyl alcohol, either of which may be employed to extract it from an aqueous solution. Even ether may be employed to extract morphine from an alkaline solution, if shaken with it immediately after adding the alkali, and before the morphine has precipitated. Morphine differs from most other alkaloids by being very soluble in potash; if a drop of weak potash be stirred with solution of a salt of morphine, the alkaloid is precipitated, but it is redissolved by a very little more potash. Ammonia does not easily redissolve it, unless ammonium chloride is present.

Crystallised morphine is $C_{17}H_{19}NO_3.H_2O$, and does not lose its water till 120° C., when it fuses, and becomes a crystalline mass on cooling. When more strongly heated, a little sublimes, but the greater part carbonises and evolves alkaline vapours. Morphine behaves like a tertiary monamine; its solutions are alkaline, and it combines with acids, like ammonia. The proportion of morphine in opium varies from 6 to 15 per cent.

Morphine hydrochloride, $C_{17}H_{19}NO_3.HCl$, or *muriate of morphia*, is the chief form in which morphine is used in medicine. It crystallises in needles with 3Aq, and is easily soluble in water and alcohol. *Morphine meconate*, the most soluble of the salts, is also used in medicine; it exists in opium.

Morphine and its salts act as powerful narcotic poisons; they are easily identified by giving a blue colour with ferric chloride (purple in the case of meconate) and a golden yellow with strong nitric acid. Morphine acts, in many cases, as a reducing agent; it liberates iodine from iodic acid in solution; it reduces potassium ferricyanide to ferrocyanide, and precipitates silver when boiled with silver nitrate. When distilled with potash, morphine yields methylamine.

Apomorphine, $C_{17}H_{17}NO_2$, is formed when morphine is heated with a large excess of strong hydrochloric acid, for some hours, to 150 C.; $C_{17}H_{19}NO_3 = C_{17}H_{17}NO_2 + H_2O$. From the hydrochloride thus obtained, sodium carbonate precipitates apomorphine as an amorphous powder, rapidly turning green in air, and then dissolving in ether with a pink colour. It is much more soluble in alcohol and ether than morphine. Apomorphine is a powerful emetic, even when injected under the skin.

Oxymorphine, or *pseudomorphine*, $C_{17}H_{19}NO_4$, is produced by warming solution of morphine hydrochloride with silver nitrite; the sparingly soluble hydrochloride gives a crystalline precipitate of oxymorphine when mixed with ammonia. This base is nearly insoluble in water, alcohol, and ether. It exists in opium.

Morphine periodide, $C_{17}H_{19}NO_3.I_4$, is obtained as a brown precipitate when solution of iodine in KI is added to morphine hydrochloride.

Codeine, or *methyl morphine*, $C_{17}H_{18}(CH_3)NO_3$, is obtained from opium by adding potash or soda to the ammoniacal filtrate from the morphine. It may be purified by crystallisation from ether. Codeine has been obtained from morphine by heating it with methyl iodide in alcoholic solution.

Codeine is easily soluble in hot water, alcohol, and ether. It crystallises from ether in anhydrous octahedra, and from water in rhombic prisms, which contain Aq. The crystals fuse under water. It is a narcotic poison, though less powerful than morphine, and amounts in opium to only about 0.5 per cent. It is strongly alkaline, gives no colour with ferric chloride, and does not reduce iodic acid like morphine. It is a tertiary monamine. When heated with caustic alkalies, it yields methylamine and trimethylamine. Heated with strong HCl to 150° C., it yields apomorphine and methyl chloride—

$$C_{17}H_{18}(CH_3)NO_3 + HCl = C_{17}H_{17}NO_2 + CH_3Cl + H_2O.$$

If it be heated to 100° C. with hydrochloric acid, it acquires Cl in place of HO, and becomes *chlorocodide*, $C_{18}H_{20}ClNO_2$, which may be precipitated from the hydrochloride by an alkali, and is reconverted into codeine by water at 140° C.

Narcotine, $C_{19}H_{14}(CH_3)_3NO_7$, is extracted from the residue left after exhausting opium with water. This is digested with acetic acid, which dissolves the narcotine, and yields it as a precipitate on adding ammonia. It may be crystallised from alcohol in prisms, which contain Aq. Narcotine, like morphine, is almost insoluble in water, but, unlike that base, it dissolves in ether, which will extract it from powdered opium, leaving the morphine. Narcotine is insoluble in potash. It is a very weak base, not alkaline, dissolving in acids, but not forming well-defined salts. It has a narcotic effect, but is not nearly so poisonous as morphine. Opium contains from 4 to 8 per cent. of narcotine, and the presence of this drug is more easily detected by testing for narcotine than for morphine, on account of the solubility of the former in ether. The material to be tested is extracted with ether, the latter evaporated off, the residue dissolved in dilute HCl, and a little *euchlorine-water* added (made by adding strong HCl to a weak solution of potassium chlorate till it has a bright yellow colour, and adding water till it is pale yellow); this produces, with narcotine, a yellow colour in the cold, becoming pink on boiling and adding more of the euchlorine-water. Narcotine was the first base extracted from opium.

When narcotine is heated with water to 250° C., it yields much trimethylamine $N(CH_3)_3$. When heated with hydriodic acid, it yields methyl iodide and *nornarcotine*, $C_{19}H_{17}NO_7$; hence, narcotine is *trimethyl nornarcotine*. The mono- and di-methyl nornarcotines have been obtained by heating narcotine with HCl. When long boiled with water, narcotine is decomposed into a new base, *cotarnine*, $C_{12}H_{13}NO_3.Aq$, which is soluble in water; and *meconin*, $C_{10}H_{10}O_4$, which is sparingly soluble in water, and has some of the properties of an alcohol. It is contained in opium to the amount of rather less than 1 per cent. This decomposition of narcotine is expressed by the equation $C_{22}H_{23}NO_7 = C_{12}H_{13}NO_3 + C_{10}H_{10}O_4$.

Opianic acid, $C_{10}H_{10}O_5$, is obtained, together with cotarnine, when narcotine is oxidised by manganese dioxide and sulphuric acid, or by dilute nitric acid. It crystallises in sparingly soluble needles, and, when heated with potash, yields meconin and the potassium salt of another crystalline acid, *hemipinic acid*, $C_{10}H_{10}O_6$; $2C_{10}H_{10}O_5 + 2KHO = C_{10}H_8K_2O_6 + C_{10}H_{10}O_4 + 2H_2O$. These two acids appear to be derivatives of protocatechuic (dihydroxybenzoic) acid, $C_6H_3(OH)_2.CO_2H$ (p. 525), hemipinic acid being *carboxylated dimethyl proto-catechuic acid*, $C_6H_2(O.CH_3)_2(CO_2H)_2$, while, in opianic acid, the aldehyd group replaces a carboxyl group, $C_6H_2(O.CH_3)_2.COH.CO_2H$.

Thebaine, $C_{19}H_{21}NO_3$, is contained in opium in small proportion; it remains in the solution from which the hydrochlorides of morphine and codeine have crystallised. This solution is mixed with ammonia, which precipitates thebaine together with some narcotine; the precipitate is dissolved in a little acetic acid, and the narcotine precipitated by tribasic lead acetate. The lead is precipitated from the filtrate by dilute sulphuric acid, after which ammonia is added to precipitate the thebaine. This alkaloid, like morphine, is insoluble in water, but dissolves in alcohol and ether, and crystallises in plates. It is insoluble in alkalies. Its alcoholic solution is alkaline. Thebaine gives a blood-red solution with strong sulphuric acid. When heated with hydrochloric acid, it yields an isomeride, *thebenine*, which gives a blue colour with sulphuric acid. Thebaine is very poisonous, producing tetanic convulsions.

Narceine, $C_{23}H_{29}NO_9$, remains in the solution from which the thebaine and narcotine have been precipitated by ammonia. This is mixed with lead acetate, to precipitate the rest of the narcotine, filtered, the lead removed by sulphuric acid, the filtrate neutralised by ammonia, and evaporated, when the narceine crystallises, leaving meconin in solution, which may be extracted by shaking with ether.

Narceine crystallises from water in prisms with 2Aq: it is soluble in alcohol, but not in ether. It is a narcotic poison. Iodine colours its solution blue.

Papaverine, $C_{21}H_{21}NO_4$, is contained, in small proportion, in the precipitate produced by excess of potash in the aqueous solution of opium. The precipitate is dissolved in ether, and shaken with dilute acetic acid: the lower layer then contains the acetates of narcotine, thebaine, and papaverine; these are again precipitated by potash, and treated with oxalic acid, which leaves the acid papaverine oxalate undissolved. Papaverine is sparingly soluble in water, but dissolves in hot alcohol and ether. It gives a violet-blue solution with strong sulphuric acid. Its poisonous properties appear to be feeble.

476. *Cinchona-alkaloids.*—The plants of the natural order *Cinchonaceæ* are remarkable for their medicinal properties. Conspicuous among them are *cinchona*, which furnishes quinine; the *coffee-tree*, which yields caffeine; and the *ipecacuanha*, which produces emetine.

Cinchona, or *Peruvian bark*, is obtained chiefly from the districts around the Andes, and owes its valuable febrifuge qualities to the presence of certain alkaloids, of which the most important are—

Quinine . . .	$C_{20}H_{24}N_2O_2$	Cinchonidine . .	$C_{20}H_{24}N_2O$
Conquinine . . .	$C_{20}H_{24}N_2O_2$	Paytine . . .	$C_{21}H_{24}N_2O_2$
Quinamine . . .	$C_{20}H_{26}N_2O_2$	Aricine . . .	$C_{23}H_{26}N_2O_4$
Cinchonine . . .	$C_{20}H_{24}N_2O$		

Of these, quinine and cinchonine are by far the most important. The different species of cinchona yield a bark containing these alkaloids in different proportions. The *yellow* bark yields from 2 to 3 per cent. of quinine, and only 0.2 or 0.3 of cinchonine; the *red* bark, about 2 per cent. of quinine and 1 per cent. of cinchonine; and the *pale* or *grey* bark, about 0.8 per cent. of quinine and 2 per cent. of cinchonine. The alkaloids exist in combination with quinic acid and with a variety of tannin known as quinotannic acid.

Quinine, $C_{20}H_{24}N_2O_2$, is prepared by boiling the bruised bark with diluted hydrochloric acid, and mixing the filtered solution with lime diffused through water, until it is alkaline. The precipitate, containing quinine, cinchonine, and colouring matter, is filtered off and boiled with alcohol, which dissolves both the alkaloids, leaving the excess of lime undissolved. A part of the alcohol is then recovered by distillation, and the solution neutralised with sulphuric acid, boiled with animal charcoal till decolorised, and filtered. On standing, quinine sulphate crystallises out, leaving the cinchonine sulphate in solution. The quinine sulphate is dissolved in water, and decomposed by ammonia, which precipitates the quinine.

Quinine crystallises in prisms containing 3Aq, which require 900 parts of cold water for solution; it dissolves easily in alcohol, ether, and chloroform. Its solutions are alkaline, and bitter. It appears to be a tertiary di-amine, because, when heated with the iodides of alcohol radicals, it yields iodides which furnish ammonium bases when decomposed by silver hydroxide; thus, methyl iodide gives $C_{20}H_{24}.CH_3.N_2O_2I$, which yields the alkaline hydroxide, $C_{20}H_{24}.CH_3.N_2O_2.OH$.

Quinine is characterised by exhibiting a beautiful blue *fluorescence* when dissolved in dilute sulphuric acid, and by producing a fine green colour when its dilute acid solutions are mixed with a little chlorine- or bromine- or euchlorine-water (see p. 597), and afterwards with ammonia. The green colour is due to *thalleiochin*, formed by the reaction

$$C_{20}H_{24}N_2O_2 + NH_3 + O_4 = C_{20}H_{27}N_3O_6.$$

Quinine is a di-acid base, but it sometimes forms salts in which it monacid; there are two hydrochlorides; $C_{20}H_{24}N_2O_2.2HCl$ is converted by water into $C_{20}H_{24}N_2O_2.HCl$, which crystallises in needles of the formula $2(C_{20}H_{24}N_2O_2.HCl).3Aq$.

Normal quinine sulphate, $C_{20}H_{24}N_2O_2.H_2SO_4.7Aq$, is soluble in 11 parts of cold water, but the *basic sulphate*, $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.8Aq$, requires 780 parts of cold water to dissolve it. This is the quinine salt generally used in medicine; it forms very light silky needles, which dissolve easily in dilute sulphuric acid, forming the *acid sulphate*, $C_{20}H_{24}N_2O_2.(H_2SO_4)_2.7Aq$, which is very soluble.

Quinine is very slightly soluble in potash, and sparingly in ammonia, though it is more soluble in NH_3 than any other cinchona alkaloid. If normal quinine sulphate be dissolved in strong acetic acid, warmed, and an alcoholic solution of iodine added gradually, thin rectangular plates are deposited on cooling, having the formula

$$C_{20}H_{24}N_2O_2.H_2SO_4.I_2.5H_2O.$$

These crystals (*herapathite*, or *artificial tourmaline*) are bronze-green by reflection, but transmit light of a pale olive colour, which is perfectly polarised, like that transmitted by tourmaline, so that, if another plate be laid upon the first, no light is transmitted when their principal axes are at right angles.

Quinidine, or *conquinine*, $C_{20}H_{24}N_2O_2$, is isomeric with quinine, and is extracted from a brown substance called *quinoidine*, or *amorphous quinine*, which is obtained from the mother-liquors of quinine sulphate, and is sold as a cheap substitute for quinine. It is also obtained in quantity from some of the inferior varieties of cinchona, such as *Cinchona cordifolia*, which yields the Carthagena bark. Quinidine forms larger prismatic crystals than quinine, and these contain only 2Aq. Its salts are more soluble than those of quinine, and they are strongly dextrorotatory for polarised light, while those of quinine are lævorotatory.

Quinicine, also isomeric with quinine, is formed by heating quinine or quinidine with dilute sulphuric acid to 130° C. It is resinous, but its salts crystallise. Its solutions are feebly dextrorotatory.

Cinchonine, $C_{20}H_{24}N_2O$, remains as sulphate in the mother-liquor from quinine sulphate (p. 598), and may be precipitated by ammonia. It is almost insoluble in water, and sparingly soluble in alcohol. Ether scarcely dissolves it, and is used to distinguish it from quinine. It crystallises from hot alcohol in anhydrous prisms, which have an alkaline reaction. The salts of cinchonine are more soluble than those of quinine, and give a much more voluminous precipitate with ammonia, which is insoluble in a large excess, and is not cleared up by shaking with ether, as in the case of quinine.

Cinchonine sulphate, $(C_{20}H_{24}N_2O)_2.H_2SO_4.2Aq$, fuses when heated, evolving an aromatic odour and becoming red. Solution of cinchonine sulphate is less strongly fluorescent than quinine sulphate. Cinchonine also differs from quinine in yielding solutions which are strongly dextrorotatory for polarised light. Cinchonine itself may be partly sublimed by a gentle heat, which is not the case with quinine.

By treating cinchonine hydrochloride with bromine, the hydrochloride of bromocinchonine, $C_{20}H_{23}BrN_2O$, is obtained. If this be precipitated by ammonia and boiled with potash, $C_{20}H_{23}BrN_2O + KHO = KBr + C_{20}H_{23}(HO)N_2O$, *hydroxycinchonine*, or *oxycinchonine*; this is metameric with quinine, but is insoluble in ether.

Cinchonidine is isomeric with cinchonine, but is strongly lævorotatory.

Cinchonicine, another isomeride, resembles quinicine in origin and properties.

When quinine, cinchonine, and the bases isomeric with them are fused with potash, they yield the *quinoline bases*, three volatile homologous bases found in coal-tar, viz., *quinoline*, C_9H_7N; *lepidine*, $C_{10}H_9N$; and *cryptidine*, $C_{11}H_{11}N$. The tarry odour on heating cinchonine is probably due to these.

477. *Caffeine* or *theine*, $C_8H_{10}N_4O_2$, or *methyl-theobromine*,

$$C_7H_7(CH_3)N_4O_2,$$

is also extracted from a plant of Cinchonaceous order, the coffee-tree

(*Caffea arabica*), the seeds of which contain about 1.5 per cent. of caffeine. It is also found in the leaves; but those of the tea-plant (*Thea*) yield more of it, the proportion in the dried leaf varying from 2 to 4 per cent.

To prepare caffeine, tea-dust is boiled with water to extract all the soluble matter, which amounts to about 30 per cent., and consists of tannin, caffeine, aromatic oil, and other bodies. The decoction is filtered, mixed with excess of lead acetate, which precipitates the tannin, again filtered, the lead precipitated by H_2S, and the filtrate from the lead sulphide evaporated to a small bulk, when the caffeine crystallises out, and may be purified by recrystallisation from alcohol. The waste tea-leaves which have been exhausted in the tea-pot will yield a considerable proportion of caffeine when treated in this way. Caffeine may be extracted from unroasted coffee-beans by grinding them, and treating them in a similar way. Caffeine may be sublimed from tea-leaves or coffee-beans by gently heating them in an evaporating dish covered with a dial-glass; one of the best processes for obtaining it is to precipitate decoction of tea with tribasic lead acetate, to evaporate the filtrate to dryness, on the steam-bath, at last, and to cautiously heat the dry residue in an evaporating dish, when the caffeine sublimes on to the cover.

Caffeine may also be extracted from raw coffee by mixing it with half its weight of slaked lime, extracting with hot alcohol, evaporating to dryness, redissolving in alcohol, filtering, diluting with water, and evaporating off the alcohol, when the oil separates and may be filtered off, and the solution deposits crystals of caffeine.

Caffeine is contained in several plants which are used in various places for chewing or preparing drinks. *Paraguay tea* is made from the leaves of one of the *Ilicaceæ*, or holly order, the *Ilex paraguayensis*, and is drunk, under the names of *maté* and *congonha*, in Paraguay, Brazil, Chili, and Peru. The leaves contain caffeine. Another beverage containing caffeine is used by the Indians of Brazil, and called Guaraná, being prepared from the seeds of the *Paullinia sorbilis*, a tree of the soap-wort order, to which the horse-chestnut belongs. The *kola-nut*, or seeds of *Cola acuminata*, used as food and medicine by the natives of West-Central Africa, contains about 2 per cent. of caffeine.

Caffeine crystallises in fine silky needles containing a molecule of water, which is expelled at 100° C. It melts at 225° C., and sublimes undecomposed. It dissolves in 90 parts of cold water, yielding a bitter solution, which is not alkaline. It is soluble in alcohol and ether, and more easily in benzene and chloroform.

Caffeine is a very weak base, its salts being decomposed by water. The hydrochlorate, $C_8H_{10}N_4O_2.HCl.2Aq$, crystallises from strong hydrochloric acid in prisms, which leave pure caffeine at 100° C. The sulphate, $C_8H_{10}N_4O_2.H_2SO_4$, is obtained in needles by adding dilute sulphuric acid to a hot alcoholic solution of caffeine. The acetate is $C_8H_{10}N_4O_2(C_2H_4O_2)_2$.

The products of oxidation of caffeine connect it closely with uric acid. Chlorine-water (or $HCl+KClO_3$) converts it into *amalic acid*, or *tetramethyl alloxantin*, $C_8(CH_3)_4N_4O_7.Aq$. In the presence of air, water, and ammonia, this yields *murexoin*, or *tetramethyl murexide*, $C_8(CH_3)_4N_5O_6(NH_4)$, which crystallises from hot water in scarlet prisms with a golden lustre. The test for caffeine is based on this: dissolve it in strong HCl, add a crystal of potassium chlorate, and evaporate to dryness. A red residue is left, which becomes purple with ammonia, and is bleached by potash.

The final product of the action of chlorine-water on caffeine is *cholestrophane*, or *dimethyl-parabanic acid*, $C_3(CH_3)_2N_2O_3$, another derivative of uric acid. When long boiled with baryta-water, caffeine is converted into *caffeidine*, $C_7H_{12}N_4O$, which is a stronger base than caffeine; $C_8H_{10}N_4O_2 + Ba(OH)_2 = C_7H_{12}N_4O + BaCO_3$.

Theobromine, $C_7H_8N_4O_2$, homologous with caffeine, and at one time believed to be isomeric with it, is extracted from the seeds of the cacao-tree (*Theobroma cacao*), which grows in Demerara. These are known as *cocoa-nibs*, and are the raw material of cocoa and chocolate. The seeds contain about 0.5 per cent. of theobromine, which may be extracted from them in the same way as caffeine from tea or coffee. It much resembles caffeine, but, when treated with hydrochloric acid and potassium chlorate, it yields *dimethyl-alloxantin*, $C_8H_2(CH_3)_2N_4O_7$. When theobromine is dissolved in ammonia and boiled with silver nitrate, a white precipitate of *silver theobromine*, $C_7H_7AgN_4O_2$, is obtained, and when this is heated with methyl iodide, it yields methyl theobromine, or caffeine—

$$C_7H_7AgN_4O_2 \ + \ CH_3I \ = \ C_7H_7(CH_3)N_4O_2 \ + \ AgI.$$

Emetine, $C_{30}H_{44}N_2O_8$, is a little-known base extracted from the root of *Cephaelis ipecacuanha*, a cinchonaceous plant much used in medicine.

478. *Strychnos-alkaloids.*—Strychnine and brucine are obtained from *nux-vomica*, the seeds of the tropical plant *Strychnos nux-vomica*, from *false angostura bark*,[*] which is the bark of the same tree, and from *Ignatia amara*, or *St. Ignatius' bean*. Nux-vomica, or *crow-fig*, contains about 1 per cent. of strychnine and 1 per cent. of brucine.

Strychnine, $C_{21}H_{22}N_2O_2$, is extracted from the crushed seeds of nux-vomica by boiling them with very dilute hydrochloric acid. The solution is mixed with milk of lime, and the precipitate filtered off and boiled with alcohol, which dissolves the strychnine and brucine, and deposits the strychnine first when evaporated. The mother-liquor is neutralised with nitric acid, when strychnine nitrate crystallises out, leaving brucine nitrate in solution.

Strychnine crystallises in rhombic prisms, which require 7000 parts of water for solution. It is insoluble in ether and in absolute alcohol, but dissolves in dilute alcohol. It is very soluble in chloroform, which is the best agent for collecting it from aqueous solutions. Its intense bitter taste is very remarkable, and may be imparted to one million parts of water (one grain in fourteen gallons). Its alcoholic solution is alkaline, and it is a monacid tertiary base, combining with methyl iodide to form *strychnine-methylium iodide*, $N_2C_{21}H_{22}O_2.CH_3I$, which yields the corresponding hydroxide base when decomposed by AgHO. But this ammonium base is not bitter, nor poisonous unless injected under the skin, when it induces paralysis. Strychnine is extremely poisonous, giving rise to tetanic convulsions. Potash precipitates strychnine from its solution in acids, and an excess does not dissolve it; the precipitate by ammonia dissolves in excess, but the strychnine crystallises out after a time. The smallest particle of strychnine may be identified by dissolving it in strong sulphuric acid and adding a minute fragment of potassium dichromate, which produces a fugitive blue-violet colour. When strychnine is warmed with dilute nitric acid, it gives a faint pink solution, which becomes scarlet on adding a particle of powdered potassium chlorate; ammonia changes this to brown, and, on evaporating to dryness, a green residue is obtained, which dissolves in water to a green solution, changed to orange by potash, and becoming green again with nitric acid. Euchlorine-water (p. 597), added to a solution of strychnine in hydrochloric acid, gives, on boiling, a fine red colour, bleached by excess, and returning when boiled.

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[*] True angostura bark is obtained from *Galipea officinalis* and *G. cusparia*, belonging to the order Rutaceæ. It is used as a febrifuge.

Brucine, $C_{23}H_{26}N_2O_4$, is precipitated by potash from the solution of brucine nitrate obtained in the extraction of strychnine. It is more soluble in water and alcohol than strychnine, and crystallises in prisms with 4Aq. Like strychnine, it is nearly insoluble in ether. It is intensely bitter and strongly basic. Nitric acid dissolves it with a fine red colour, which becomes violet on adding stannous chloride. When distilled with MnO_2 and H_2SO_4, brucine yields methyl alcohol.

479. *Aconitine*, $C_{33}H_{43}NO_{12}$, is extracted from the root of *Aconitum napellus*, a plant of the Ranunculaceous or buttercup order, known as *monk's hood*, *blue rocket*, and *wolf's bane*. The root has often been scraped and eaten by mistake for *horse-radish* (*Cochlearia armoracia*, a cruciferous plant), but the two roots are really very unlike, and the scrapings of monk's hood become pink when exposed to air, while those of horse-radish remain white. To extract the aconitine, the scrapings of the root are boiled with alcohol mixed with a little tartaric acid; the solution is evaporated below 60° C.; the dry residue is dissolved in water and shaken with ether, which removes some foreign matters; the aqueous layer is then precipitated by hydrosodium carbonate; the precipitated aconitine is dissolved in dilute sulphuric acid and precipitated by ammonia. It may be crystallised from alcohol in plates which are anhydrous, and forms well-defined salts. Aconitine is one of the most poisonous alkaloids, and, as yet, no trustworthy chemical test for it is known, so that the toxicologist is obliged to place a little of the suspected substance on the tongue, when aconitine produces a numbing tingling feeling lasting for some time. When heated with potash, aconitine yields potassium benzoate and *aconine*, a new base.

Pseudaconitine, $C_{27}H_{37}NO_5$, is a poisonous alkaloid obtained from *Aconitum ferox*, an Indian plant of the same natural order. Pseudaconitine yields no crystalline salt except the nitrate, and crystallises with a molecule of water. Heated with potash, it yields *pseudaconine*, $C_{27}H_{41}NO_8$, and the potassium-salt of dimethyl dihydroxybenzoic (or dimethyl protocatechuic) acid (p. 525).

The preparations sold as aconitine are often impure bases of very variable quality.

Veratrine, $C_{37}H_{53}NO_{11}$, is extracted from the root of white hellebore (*Veratrum album*) and from the seeds of *Veratrum sabadilla*, plants of the natural order Colchicaceæ. The alkaloid is present in very minute quantity. It is extracted by digesting the root with alcohol containing a little tartaric acid, evaporating the alcohol from the filtered solution, dissolving the residue in water, liberating the alkaloid by caustic soda, and shaking with ether, which dissolves it. The ethereal layer leaves the alkaloid when evaporated. Veratrine is characterised by its power to cause violent sneezing when a particle of the powder is drawn into the nose. It dissolves in HCl, and the solution becomes red when gently heated. Strong H_2SO_4 gives a yellow solution passing into carmine-red, and becoming purple with bromine-water. *Ceradine*, $C_{32}H_{49}NO_9$, is another alkaloid which causes sneezing, and is extracted from Cevadilla seeds (*Veratrum sabadilla*). *Veratralbine*, $C_{28}H_{43}NO_5$, *jervine*, $C_{26}H_{37}NO_3$, *pseudojervine*, $C_{29}H_{43}NO_7$, and *rubijervine*, $C_{26}H_{43}NO_2$, are also extracted from the veratrums. These plants are chiefly used for poisoning vermin.

Bebeerine, $C_{19}H_{21}NO_3$, is extracted from the bark of the bibiru-tree, a tree of the laurel order, which grows in British Guiana, and yields the *green-heart* wood used in ship-building, because it resists the attacks of marine animals. It is amorphous, insoluble in water, but soluble in alcohol. The sulphate, $(C_{19}H_{21}NO_3)_2.H_2SO_4$, is sometimes used in medicine instead of quinine sulphate.

Berberine, $C_{20}H_{17}NO_4$, is obtained from the root of the barberry (*Berberis vulgaris*), and from calumba-root (*Cocculus palmatus*) and false calumba-root (*Menispermum fenestratum*), both belonging to the Menispermaceæ. Berberine crystallises in yellow needles with 6Aq, and forms yellow salts. It is soluble in water.

Piperine, $N(C_5H_{10})''(C_{12}H_9O_3)$, is a feeble base extracted by alcohol from white pepper, the ripe fruit of *Piper nigrum* (the unripe fruit is black pepper). It crystallises in plates, which are insoluble in water, but soluble in ether. The alcoholic solution tastes hot. When boiled with potash—

$$N(C_5H_{10})''(C_{12}H_9O_3) + KHO = \underset{\textit{Piperidine.}}{N(C_5H_{10})''H} + \underset{\textit{Potassium piperate.}}{C_{12}H_9O_3.OK}$$

Piperidine is a liquid secondary monamine, boiling at 106° C., and smelling of pepper and ammonia; it is soluble in water, forms crystalline salts, and behaves like other secondary amines in yielding tertiary amines and ammonium bases. When heated to 300° C. with strong H_2SO_4, it yields pyridine, C_5H_5N, which may be reconverted into piperidine by nascent hydrogen, furnished by tin and HCl. *Piperic acid*, $C_{12}H_{10}O_4$, is precipitated from the potassium-salt by hydrochloric acid, and crystallises in yellow needles from alcohol. When fused with potash, it yields the carbonate, oxalate, acetate, and protocatechuate, the last indicating that it is a benzene derivative.

480. *Cocaine*, $C_{17}H_{21}NO_4$, is extracted from the leaves of *Erythroxylon coca*, a Peruvian stimulant. It crystallises in prisms containing Aq, and dissolves in alcohol. It is used in ophthalmic affections.

Physostigmine, or *eserine*, $C_{15}H_{21}N_3O_2$, is obtained from the Calabar bean, the seed of a Papilionaceous plant. It is sparingly soluble in water, but dissolves in alcohol, is strongly alkaline, and very poisonous. It has the property of contracting the pupil of the eye.

Colchicine, $C_{17}H_{19}NO_5$, occurs in meadow saffron, *Colchicum autumnale* (belonging to the same order as the Veratrums); much used as a remedy in gout. It is a very feeble base, soluble in water and alcohol, and does not crystallise.

Cytisine, $C_{24}H_{27}N_3O$, is the poisonous alkaloid contained in the seeds of *Cytisus laburnum*, a Papilionaceous plant.

Chelidonine, $C_{19}H_{17}NO_4$, has been extracted from celandine (*Chelidonium majus*), a plant of the Poppy order. It may be remarked that the formula of chelidonine nearly resembles that of morphine, obtained from a plant belonging to the same natural order.

Delphinine, $C_{24}H_{35}NO_2$, is the poisonous alkaloid contained in larkspur or stavesacre (*Delphinium staphisagria*), the seeds of which are used for destroying vermin (aconite belongs to the same order).

Pilocarpine, $C_{11}H_{16}N_2O_2$, is extracted from the leaves of *Pilocarpius pennatifolius*, a plant of the Rue order. The base itself is not crystalline, but the hydrochloride and nitrate are crystalline salts, which are used in medicine.

Jaborandine, $C_{10}H_{12}N_2O_3$, is another alkaloid obtained from the same source.

CYANOGEN AND ITS COMPOUNDS.

481. In the beginning of the last century, a manufacturer of colours at Berlin accidentally obtained a blue powder when precipitating sulphate of iron with potash. This substance was used as a colour, under the name of *Prussian blue*, for several years, before any explanation of its production was attempted, or even before the conditions under which it was formed were exactly determined. In 1724 it was shown that Prussian blue could be prepared by calcining dried animal matters with potashes and mixing the aqueous solution of the calcined mass, first with sulphate of iron and afterwards with hydrochloric acid; but the most important step towards the determination of its composition was made by Macquer, who found that, by boiling it with an alkali, Prussian blue was decomposed, yielding a residue of red oxide of iron, and a solution which reproduced the blue when mixed with a salt of iron, from which he inferred that the colour was a compound of the oxide of iron with an acid for which the alkali had a more powerful attraction—a belief confirmed, in 1782, by Scheele's observations, that when an alkaline solution prepared for making the blue was exposed to the air, or to the action of carbonic acid, it lost the power of furnishing the colour, but the escaping vapour struck a blue on paper impregnated with oxide of iron. Scheele also prepared the acid in a pure state, and it soon after obtained the name of *prussic acid.*

In 1787, Berthollet found prussic acid to be composed of carbon, hydrogen, and nitrogen, but he also showed that the power of the alkaline liquor to produce Prussian blue depended upon the presence of a yellow salt crystallising in octahedra, and containing prussic acid, potash, and oxide of iron, though the latter was so intimately bound up with the other constituents that it could not be separated by those substances which are usually employed to precipitate iron.

Porrett, in 1814, applying the greatly increased resources of chemistry to the investigation of this subject, decomposed Prussian blue with baryta, and subsequently removed the baryta from the salt thus obtained by means of sulphuric acid, when he obtained a solution of the acid, which he named *ferruretted chyazic acid.*

In 1815, Gay-Lussac, having boiled Prussian blue (or prussiate of iron, as it was then called) with red oxide of mercury and water, and crystallised the so-called prussiate of mercury, exposed it, in the dry state, to the action of heat, and obtained a gas having the composition CN, which was called *cyanogen*,* in allusion to its connexion with Prussian blue. It was then seen that the substance which had been called ferruretted chyazic acid contained iron and the elements of cyanogen, whence it was called *ferrocyanic acid*, and its salts were spoken of as ferrocyanates. Robiquet first obtained this acid in the crystallised state, having the composition $C_6H_4N_6Fe$; and since it was found that, when brought in contact with metallic oxides, it exchanged the H_4 for an equivalent quantity of the metal, according to the equation—

$$H_4.C_6N_6Fe + 2M''O = M_2''.C_6N_6Fe + 2H_2O,$$

it was concluded that the C_6N_6Fe composed a distinct group or radical, which was named *ferrocyanogen* (Fcy) the acid being called *hydroferrocyanic acid*, and the salts *ferrocyanides.*

482. *Cyanogen compounds containing the group* CN.—*Cyanogen*, $(CN)_2$ or NC.CN, is obtained by heating mercuric cyanide in a glass tube or retort (fig. 284) and collecting the gas over mercury; $Hg(CN)_2 = Hg + (CN)_2$; the metallic mercury collects in globules on the cool glass. The whole of the cyanogen is not obtained, part being converted into a brown solid called *paracyanogen*, which is left behind. This is polymeric with cyanogen, into which it may be converted by a high temperature.

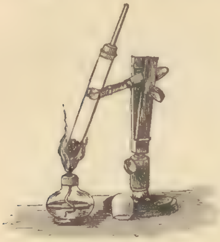

Fig. 284.

Cyanogen is identified by its remarkable odour, and by its burning with a pink flame edged with green. Its sp. gr. is 1.806 (air = 1), and it may therefore be collected by displacement of air. It is easily liquefied by a pressure of 4 atmospheres at 15° C. and 1½ atmosphere at 0° C. Liquid cyanogen has sp. gr. 0.87, and solidifies to a crystalline mass at − 34° C. Water dissolves about 4 volumes of cyanogen, yielding a solution which soon decomposes, depositing a brown flocculent substance termed *azulmic acid*, $C_4N_5H_5O$. The solution is then found to contain ammonium salts, especially the carbonate, formate, and oxalate, together with urea. The first reaction between cyanogen and water, on standing, probably resembles that between chlorine and KHO in the cold, viz., $Cl_2 + 2KHO = KCl + KClO + H_2O$; the reaction in the case of cyanogen being $(CN)_2 + H_2O = HCN + H(CN)O$, producing hydrocyanic, HCN, and cyanic, HCNO, acids. The cyanic acid, acting upon water, produces hydro-ammonium carbonate; $HCNO + 2H_2O = NH_4HCO_3$. Hydrocyanic acid, in contact with water, yields ammonium formate; $HCN + 2H_2O = HCO_2NH_4$. Cyanogen, with water, yields ammonium oxalate; $(CN)_2 + 4H_2O = C_2O_4(NH_4)_2$. Cyanic acid, with ammonia, yields urea; $HCNO + NH_3 = (NH_2)_2CO$. The azulmic acid appears to result from a reaction between cyanogen, ammonia, and water; $2(CN)_2 + NH_3 + H_2O = C_4H_5N_5O$; it may be prepared by passing cyanogen into dilute ammonia, and heating in a closed vessel. When dry ammonia gas acts upon cyanogen gas, a black substance is produced, which is called *hydrazulmin;* $2NH_3 + 2(CN)_2 = C_4H_6N_6$. This appears to be *azulmamide*, for, when acted on by water, it yields azulmic acid and ammonia; $C_4H_6N_6 + H_2O = C_4H_5N_5O + NH_3$.

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* From κυάνεος, blue.

In the preceding reactions, cyanogen exhibits the mutability which is generally observed in organic groups, but in some cases it exhibits a stability which allows it to be compared with the halogens chlorine and bromine. Thus, potassium and sodium take fire in cyanogen gas when gently heated, producing their respective cyanides; $K_2 + (CN)_2 = 2KCN$; cyanogen, acting on solution of potash, yields potassium cyanide and cyanate; $(CN)_2 + 2KHO = KCN + KCNO + H_2O$, just as chlorine yields the chloride and hypochlorite—

$$Cl_2 + 2KHO = KCl + KClO + H_2O.$$

Cyanogen combines with hydrogen, under the influence of the silent electric discharge, to form hydrocyanic acid, $H(CN)$, which forms cyanides by exchanging its hydrogen for metals, just as hydrochloric acid forms chlorides; but the cyanides of potassium and sodium are much less stable compounds than the corresponding chlorides. When boiled with water, the alkaline cyanides are converted into alkaline formates, the nitrogen being evolved as ammonia, and the carbon converted into the carboxyl or oxatyl group; *e.g.*,

$$KCN''' + 2H_2O = KCO''(OH)' + NH_3.$$

The facility with which the CN group is transformed by hydrolysis into the CO_2H group is of very great importance in organic research, since it is often easy to introduce the CN group into an organic molecule, and, by afterwards converting it into CO_2H, to effect the synthetical formation of an organic acid. Moreover, since the carbon of the added cyanogen is not evolved, but only the nitrogen, the new acid will belong to the next higher carbon series. Thus, methyl alcohol, $CH_3.OH$, may be converted into methyl cyanide, $CH_3.CN$, and methyl cyanide into acetic acid, $CH_3.CO.OH$ or $C_2H_4O_2$, the acid of the ethyl series.

Cyanogen is produced in small quantity by the direct union of carbon and nitrogen at the extremely high temperature of the electric spark; but to produce it in quantity, one, at least, of its elements must be in the form of a compound; thus, if ammonia be passed over red-hot charcoal, ammonium cyanide is produced; $4NH_3 + C_3 = 2NH_4CN + CH_4$; again, if acetylene is mixed with nitrogen and *sparked*, hydrocyanic acid is formed, $C_2H_2 + N_2 = 2HCN$. If one of the alkali-metals be present, nitrogen is much more easily converted into cyanogen; potassium cyanide may be obtained by passing nitrogen through an iron tube containing a heated mixture of charcoal and potassium—

$$N_2 + C_2 + K_2 = 2KCN.$$

In place of the costly potassium, the materials for making it, viz., potassium carbonate and charcoal, may be used; $K_2CO_3 + C_4 + N_2 = 2KCN + 3CO$. A better yield is obtained by employing a compound of nitrogen with carbon, such as refuse horn or cuttings of hides and old leather, which are rich in nitrogen.

On a large scale, potassium cyanide is made in this way, but, as it cannot be crystallised easily, it is converted into the ferrocyanide, which is the source whence all cyanogen compounds are obtained.

483. *Potassium ferrocyanide*, or *yellow prussiate of potash*—

$$K_4C_6N_6Fe.3Aq, \text{ or } (KCN)_2.CN.Fe''.CN.(KCN)_2 + 3Aq,$$

is manufactured by melting potashes (potassium carbonate) in a cast-iron pot provided with a lid and a stirrer, and adding any cheap material containing carbon and nitrogen, such as old leather. Sometimes the animal matter is distilled for the sake of the ammonia, and the remaining charcoal rich in nitrogen is used for making ferrocyanide. The fused mass, which contains potassium cyanide, is treated with water, and digested with finely ground spathic iron ore (ferrous carbonate), which gradually dissolves, and the liquid, when evaporated, yields crystals of potassium ferrocyanide; $6KCN + FeCO_3 = K_4C_6N_6Fe + K_2CO_3$. It crystallises in yellow four-sided pyramids, which are often three or four inches in diameter at the base. It dissolves in twice its weight of boiling and in four times its weight of cold water, but is insoluble in alcohol. The aqueous solution assumes a darker yellow colour when exposed to air for some time, oxygen being absorbed and potassium ferricyanide produced in small quantity. The neutral solution then becomes slightly alkaline from formation of potash.

Crystallised ferrocyanide does not lose water till 60° C., when it gradually becomes white and opaque. At 100° C. it may be dried completely, though with difficulty unless finely powdered and heated in a current of dried air. When the undried salt is moderately heated, it evolves ammonia and hydrocyanic acid, and becomes brown. The thoroughly dried salt does not evolve ammonia, but fuses at a high temperature, evolving nitrogen, and leaving a residue of potassium cyanide and iron carbide; $K_4C_6N_6Fe = N_2 + 4KCN + FeC_2$.

Nearly all acids decompose the ferrocyanide, evolving hydrocyanic acid, and producing compounds containing cyanogen and iron, which become blue when exposed to air, from the formation of Prussian blue and similar compounds. It is for this reason that the yellow crystals become blue and green when exposed to the air of a laboratory. Oxidising agents convert the ferrocyanide into ferricyanide, as will be seen farther on. With a large number of metallic salts, the ferrocyanide gives precipitates, so that it is an indispensable test. It is also largely employed in the manufacture of colours, and in dyeing and calico-printing. The constitution and chemical relations of the ferrocyanides will be better understood later in the history of cyanogen compounds.

Hydrocyanic acid, HCN, has been described in the section on acids (p. 538).

Potassium cyanide, KCN, or KCy, is prepared by fusing, in an iron crucible, a mixture of well-dried potassium ferrocyanide (8 parts) with dried potassium carbonate (3 parts)—

$$K_4Cy_6Fe + K_2CO_3 = 5KCy + KCyO + Fe + CO_2.$$

As soon as the escape of CO_2 has ceased, and the metallic iron has subsided, the clear fused mixture of cyanide and cyanate of potassium is poured into an iron mould. The presence of cyanate does not interfere with most of the uses of the cyanide; its quantity may be diminished by adding some powdered charcoal to the mixture. A purer product is obtained, though less economically, by fusing the dried ferrocyanide alone (see above), and crystallising the product by dissolving in hot alcohol. The purest potassium cyanide is made by passing vapour of hydrocyanic acid into solution of potash in absolute alcohol, when the cyanide is deposited in small octahedral crystals.

Potassium cyanide, as met with in commerce, is in white opaque lumps, and contains about 60 per cent. of cyanide, the rest being cyanate and carbonate. When exposed to air, it deliquesces, and smells of hydrocyanic acid and ammonia, the former being produced from the cyanide, and the latter from the cyanate, by the action of water

$$(1)\ KCN + H_2O = KHO + HCN. \qquad (2)\ KCNO + 2H_2O = NH_3 + KHCO_3.$$

It dissolves very readily in water, yielding a strongly alkaline solution, which evolves HCy and NH_3 when boiled, and becomes a solution of potassium formate; $KCN + 2H_2O = NH_3 + HCO_2K$. When the commercial cyanide is boiled with moderately strong alcohol, the cyanide, together with a little cyanate, is dissolved, and may be crystallised from the solution, while the carbonate is left undissolved. Potassium cyanide fuses at a low red heat, becoming very fluid; it then absorbs oxygen from the air, forming cyanate. This disposition to combine with oxygen causes it to act as a powerful reducing agent upon metallic oxides; tin-stone is assayed by fusing it with potassium cyanide, when a button of tin collects at the bottom—

$$SnO_2 + 2KCy = Sn + 2KCyO.$$

When heated with potassium nitrate or chlorate, it causes a violent explosion, from evolution of CO_2 and N.

Pure potassium cyanide is alkaline, but does not effervesce with acids, like the commercial cyanide. Solution of potassium cyanide dissolves silver chloride and iodide, which leads to its use in electro-plating and in photography, while its property of dissolving silver sulphide is useful in cleaning gold and silver. It is one of the most dangerous poisons.

Potassium cyanide is sometimes obtained in considerable quantity from the blast-furnaces of ironworks, being formed from the potassium carbonate in the ash of the fuel.

Ammonium cyanide, NH_4CN, may be sublimed in cubes by heating a mixture of mercuric cyanide and ammonium chloride. It undergoes dissociation, at 36° C., into NH_3 and HCN, which recombine at lower temperatures. It is very soluble in water and alcohol, and smells of hydrocyanic acid and ammonia. When kept, it becomes brown, azulmin being produced (p. 604). Ammonium cyanide is produced when ammonia is passed over red-hot charcoal, marsh gas being also formed; $4NH_3 + C_3 = 2NH_4CN + CH_4$. It is also formed by passing a mixture of ammonia and carbonic oxide through a red-hot porcelain tube; $2NH_3 + CO = NH_4CN + H_2O$.

The *cyanides* of *barium*, *strontium*, and *calcium* are less soluble than the alkaline cyanides, and are easily decomposed by carbonic acid. *Zinc cyanide*, $ZnCy_2$, is precipitated by KCy from $ZnSO_4$; it dissolves in KCy, forming $ZnCy_2(KCy)_2$, which crystallises in octahedra. *Nickel cyanide*, $NiCy_2$, obtained in a similar way, forms a pale green precipitate, readily soluble in excess, forming $NiCy_2(KCy)_2$, from which hydrochloric acid reprecipitates the nickel cyanide—

$$NiCy_2(KCy)_2 + 2HCl = NiCy_2 + 2KCl + 2HCy.$$

If the solution of nickel cyanide in potassium cyanide be heated with mercuric oxide, nickel oxide is precipitated; $NiCy_2(KCy)_2 + HgO = HgCy_2(KCy)_2 + NiO$. This reaction is important in quantitative analysis. Nickel cyanide is remarkable for its insolubility even in boiling hydrochloric acid.

484. *Cobalt cyanide*, $CoCy_2$, is precipitated of a reddish-brown colour when potassium cyanide is added to cobalt nitrate; it dissolves easily in excess of potassium cyanide, forming *potassium cobaltocyanide*, $K_4(CoCy_6)$, which may be obtained in red deliquescent crystals by adding alcohol. This compound corresponds to potassium ferrocyanide, $K_4(FeCy_6)$, but is far less stable; when exposed to air, or boiled with water, it undergoes oxidation, the cobaltous compound being converted into a cobaltic compound, the *potassium cobalticyanide*—

$$2K_4(Co''Cy_6) + O + H_2O = 2K_3(Co'''Cy_6) + 2KHO.$$

The potassium cobalticyanide is a pale yellow salt, its solution being nearly colourless, so that the brown solution formed at first when KCy in excess is added to a cobalt salt gradually becomes pale yellow when boiled in contact with air. This solution, when mixed with hydrochloric acid in excess, yields *hydrocobalticyanic acid*, H_3CoCy_6, which is soluble, forming a distinction between cobalt and nickel. When both metals are present, the addition of HCl to the solution in excess of KCy produces a yellowish-green precipitate of *nickel cobalticyanide*, $Ni_3(CoCy_6)_2$, which is decomposed by boiling with potash, the nickel being precipitated as hydrate, and the cobalt passing into solution as potassium cobalticyanide; $Ni_3(CoCy_6)_2 + 6KHO = 3Ni(HO)_2 + 2K_3CoCy_6$. The solution of potassium cobalticyanide is not decomposed by digestion with mercuric oxide (to precipitate the nickel), but a solution of mercurous nitrate gives a white precipitate of *mercurous cobalticyanide*, $Hg_3Co_2Cy_6$, which is converted into oxide of cobalt when heated in air.

The potassium cobalticyanide may be obtained in crystals; it is analogous to, and isomorphous with, the potassium ferricyanide, to be presently described. *Hydrocobalticyanic acid* is prepared by mixing a strong solution of the potassium-salt with sulphuric acid and alcohol, when K_2SO_4 is precipitated, and the solution yields colourless crystals of $H_6(CoCy_6)_2.H_2O$, which is a very stable and powerful acid. Potassium cobalticyanide gives, with ferrous salts, a white precipitate of *ferrous cobalticyanide*, $Fe_3(CoCy_6)_2$; and with cobalt salts a red precipitate of *cobaltous cobalticyanide*, $Co''_3(Co'''Cy_6)_2.14Aq$, which loses its water at 200° C., and becomes blue.

485. *Cyanogen and iron.—Ferrous cyanide*, $Fe(CN)_2$, or $FeCy_2$, is obtained (apparently in combination with some KCy) as a red-brown precipitate, by adding potassium cyanide to a ferrous salt; it dissolves when boiled with an excess of the cyanide, and the solution, when evaporated, deposits yellow crystals of potassium ferrocyanide—

$$FeCy_2 + 4KCy = K_4FeCy_6.$$

This might be regarded as $4KCy.FeCy_2$, but the iron cannot be detected by any of the tests for that metal; thus, ammonium sulphide, which produces a black precipitate in ferrous salts, does not change the ferrocyanide; moreover, the K_4 may be exchanged for hydrogen or for other metals without affecting the iron and cyanogen, leading to the conclusion that the group $FeCy_6$ contains the iron in a state of intimate association with the cyanogen, so that its ordinary properties are lost. Again, the ferrocyanide is not poisonous, so that it cannot be believed to contain potassium cyanide.

Hydric ferrocyanide, or *hydroferrocyanic acid*, H_4FeCy_6, is prepared by mixing a cold saturated solution of potassium ferrocyanide with an equal volume of strong hydrochloric acid. It forms a white crystalline precipitate, soluble in water, but not in HCl. If it be drained, dissolved in alcohol, and ether added, it may be obtained in large crystals. It is a strong acid. When exposed to air, it absorbs oxygen, and evolves hydrocyanic acid, leaving a residue of *Prussian blue*, or *ferric ferrocyanide*, $Fe_4(FeCy_6)_3$. The acid is decomposed by boiling its solution, into hydrocyanic acid and *ferrous* ferrocyanide, $Fe_2(FeCy_6)$, which is white, but becomes blue when exposed to air—

$$3H_4FeCy_6 = 12HCy + Fe_2(FeCy_6).$$

These changes are applied to produce blue patterns in calico-printing.

Hydroferrocyanic acid is *tetrabasic*, its four atoms of hydrogen admitting of replacement by a metal to form a ferrocyanide. The group $FeCy_6$, *ferrocyanogen*, Fcy or Cfy, is a tetrad group, consisting of ferrous iron, which is diad, Fe'', and six monad cyanogen groups, $(CN)'$, leaving four vacant *bonds*.

Prussian blue, or *ferric ferrocyanide*, $Fe'''_4Fcy^{iv}_3$, is prepared by adding potassium ferrocyanide to a solution of ferric chloride, or ferric sulphate; $2Fe_2Cl_6 + 3K_4Fcy = Fe_4Fcy_3 + 12KCl$. When washed and dried, it is a dark-blue amorphous body, which assumes a coppery lustre when rubbed. It cannot be obtained perfectly free from water, always retaining about 20 per cent. $(Fe_4Fcy_3 + 12Aq)$. On heating, the water decomposes it, hydrocyanic acid and ammonia being evolved, and ferric oxide left. The water appears essential to the blue colour, for strong sulphuric acid converts it into a white powder, becoming blue again on adding water. Strong hydrochloric acid dissolves Prussian blue, forming a brown solution, which gives a blue precipitate with water. Oxalic acid dissolves it to a blue solution, used as an ink. Some ammonium salts, such as acetate and tartrate, also dissolve it. Alkalies destroy the blue colour, leaving ferric hydrate and a solution of an alkaline ferrocyanide—

$$Fe_4Fcy_3 + 12KHO = 2Fe_2(HO)_6 + 3K_4Fcy.$$

This is turned to account, in calico-printing, for producing a buff or white pattern upon a blue ground. The stuff having been dyed blue by passing, first through solution of a ferric salt, and afterwards through potassium ferrocyanide, the pattern is discharged by an alkali, which leaves the brown ferric hydrate capable of being removed by a dilute acid, when the stuff has been rinsed, so as to leave the design white. Prussian blue is present in large quantity in many black silks, and may be extracted by heating with hydrochloric acid, and precipitating the brown solution with water.

Soluble Prussian blue, or *potassio-ferric ferrocyanide*, $K_2Fe'''_2(Fcy)^{iv}_2$, is formed when solution of ferric chloride or sulphate is poured into potassium ferrocyanide, so that the latter may be present in excess during the reaction; $Fe_2Cl_6 + 2K_4Fcy = K_2Fe_2Fcy_2 + 6KCl$. This blue is insoluble in the liquid containing saline matter, but dissolves as soon as the latter has been removed by washing. The addition of an acid or a salt reprecipitates it. By decomposing soluble Prussian blue with ferrous sulphate, a blue precipitate of *ferroso-ferric ferrocyanide*, $Fe''Fe'''_2Fcy_2$, is obtained, which is erroneously called Turnbull's blue (*ferrous ferricyanide*).

Potassio-ferrous ferrocyanide, $K_2Fe''Fcy$, is obtained as a white precipitate when a solution of a ferrous salt quite free from ferric salt is added to potassium ferrocyanide quite free from ferricyanide; $FeSO_4 + K_4Fcy = K_2SO_4 + K_2FeFcy$. The ferrous solution may be prepared by placing some iron filings in a stoppered bottle and filling it up with a strong solution of sulphurous acid; after a few minutes, the solution of ferrous hyposulphite (p. 212) is poured (through a filter, if necessary) into a weak freshly prepared solution of potassium ferrocyanide. The precipitate is snow-white, and remains so for some time at the bottom of the liquid, but, if it be exposed to air, it eagerly absorbs oxygen and becomes blue; $6K_2FeFcy + O_3 = 3K_4Fcy + Fe_4Fcy_3 + Fe_2O_3$. Oxidising agents, such as chlorine-water and nitric acid, change it at once into Prussian blue. When potassium ferrocyanide is added to ordinary ferrous sulphate, a light-blue precipitate is obtained, which is a mixture of K_2FeFcy with Prussian blue formed from the ferric sulphate present in the ordinary salt. In making the Prussian blue of commerce, this precipitate is oxidised by solution of chloride of lime (p. 160), and afterwards washed with dilute HCl to remove Fe_2O_3.

Calcium chloride gives, with potassium ferrocyanide, a white crystalline precipitate of *potassio-calcium ferrocyanide*, K_2CaFcy, which is insoluble in acetic acid, but dissolves in HCl, and is reprecipitated by ammonia. *Potassio-barium ferrocyanide*, $K_2BaFcy.3Aq$, is precipitated in a similar way. *Manganese ferrocyanide*, Mn_2Fcy, is a white precipitate. *Zinc ferrocyanide*, Zn_2Fcy. is also a white precipitate. When potassium ferrocyanide is added to a zinc-salt mixed with excess of ammonia, a white crystalline precipitate of *ammonio-zinc ferrocyanide* is obtained. *Nickel ferrocyanide*, Ni_2Fcy, is a pale green precipitate. *Cobalt ferrocyanide*, Co_2Fcy, forms a pale blue-green precipitate. *Uranic ferrocyanide*, U_4Fcy_3 (?), is a rich brown-red precipitate. *Cupric ferrocyanide*, Cu_2Fcy, is also obtained as a brown-red precipitate by adding potassium ferrocyanide to cupric sulphate; it forms the colour known as *Hatchett's brown*. Its formation is a delicate test for copper, a very dilute solution giving a pink colour with the ferrocyanide.

Silver ferrocyanide, Ag_4Fcy, is obtained as a white precipitate from silver nitrate and potassium ferrocyanide; it is insoluble in dilute nitric acid, like silver chloride, but it is also insoluble in ammonia, which is the case with few silver salts. When boiled with nitric acid, it is converted into the red-brown *silver ferricyanide*, which is soluble in ammonia. When silver ferrocyanide is boiled with ammonia, it deposits metallic silver and ferric oxide, leaving silver cyanide and ammonium cyanide in solution—

$$2Ag_4FeCy_6 + 6NH_3 + 3H_2O = Ag_2 + Fe_2O_3 + 6AgCy + 6NH_4Cy.$$

A similar change takes place on boiling with potash, the precipitate becoming black.

Ferric cyanide, Fe_2Cy_6, is very unstable. When KCy is added to ferric chloride, the solution soon becomes turbid, depositing ferric hydrate and evolving HCy; $Fe_2Cy_6 + 6H_2O = Fe_2(HO)_6 + 6HCy$.

Potassium ferricyanide, or *ferridcyanide*, or *red prussiate of potash*,

$$Fe_2Cy_6.6KCy, \text{ or } (K_3Cy_6Fe''')_2, \text{ or } (KCN)_3.(CN)_3Fe'''_2(CN)_3(KCN)_3.$$

is prepared by the action of chlorine upon potassium ferrocyanide; $2K_4Fe''Cy_6 + Cl_2 = (K_3Fe'''Cy_6)_2 + 2KCl$. Chlorine gas is passed into the solution of ferrocyanide until a little of the solution tested with ferric chloride no longer gives a blue precipitate. On the small scale, chlorine-water may be added to the ferrocyanide. The yellow colour is changed to greenish-yellow, and the solution, when evaporated and cooled, deposits dark red prisms of the ferricyanide. It is very soluble in water, yielding a dark yellowish-green solution, but is nearly insoluble in alcohol. The aqueous solution is slowly decomposed by exposure to light, depositing a blue precipitate, and becoming partly converted into ferrocyanide. If the solution be mixed with acetic acid, and heated, it deposits a blue precipitate, a reaction which is turned to account in dyeing. Solution of potassium ferricyanide, rendered alkaline by potash, acts as a powerful oxidising agent, becoming reduced to ferrocyanide; $(K_3Fe'''Cy_6)_2 + 2KHO = 2K_4Fe''Cy_6 + H_2O + O$. Such a solution converts chromic oxide into potassium chromate, and bleaches indigo, whence it is used as a *discharge* in calico-printing, for white patterns on an indigo ground. Potassium ferricyanide is also reduced to ferrocyanide when boiled with potassium cyanide—

$$(K_3Fe'''Cy_6)_2 + 2KCN + 2H_2O = 2K_4Fe''Cy_6 + HCN + NH_3 + CO_2.$$

Hydric ferricyanide, or *hydroferricyanic acid*, $(H_3Fe'''Cy_6)_2$, is obtained by decomposing lead ferricyanide with sulphuric acid, not in excess. It may be crystallised in brown needles by evaporation *in vacuo*. Its solution is decomposed by boiling, with evolution of HCy and separation of a blue precipitate. Hydroferricyanic acid is *hexabasic*, the six atoms of hydrogen being replaced by metals to form ferricyanides. The group Fe_2Cy_{12}, *ferricyanogen*, or *ferridcyanogen*, Fdcy or Cfdy, is a hexad group consisting of two atoms of triad (ferric), Fe''', and twelve atoms of monad cyanogen, $(CN)'$, leaving six vacant bonds. Potassium ferricyanide may be regarded as containing two groups of $K_3C_3N_3$ linked together by ferric cyanide, Fe_2Cy_6, whilst the ferrocyanide contains two groups of $K_2C_2N_2$ linked together by ferrous cyanide, $FeCy_2$.

Ferrous ferricyanide, or *Turnbull's blue*, $Fe''_3Fe'''_2Cy_{12}$.—Whilst potassium ferrocyanide gives a light blue precipitate with common ferrous sulphate, the ferricyanide gives a dark blue precipitate resembling Prussian blue. This contains the same proportions of iron and cyanogen as the ferroso-ferric ferrocyanide, $Fe''Fe'''_2(Fe''Cy_6)_2$, and it is sometimes regarded as identical with it, on the supposition that the ferrous sulphate reduces the ferricyanide to ferrocyanide. Ferric salts give no precipitate with the ferricyanide, but only a dark brown solution, probably containing ferric ferricyanide, which yields a blue precipitate of ferrous ferricyanide with reducing agents such as sulphurous acid, and is used as a test.

Lead ferricyanide, $Pb_3Fe_2Cy_{12}.16Aq$, is deposited in red-brown crystals on mixing strong solutions of lead nitrate and potassium ferricyanide. *Silver ferricyanide*, $Ag_6Fe_2Cy_{12}$, has been already mentioned as a red-brown precipitate formed by boiling the ferrocyanide with dilute nitric acid. Cold potash converts it into black Ag_2O and potassium ferricyanide; on boiling, the black changes to pink; $3Ag_2O + K_6Fe_2Cy_{12} = 6AgCy + 6KCy + Fe_2O_3$. The pink precipitate is a compound of AgCy with silver ferricyanide, which may also be obtained by boiling silver ferricyanide with silver oxide; $Ag_6Fe_2Cy_{12} + 3Ag_2O = Fe_2O_3 + 12AgCy$, which combines with undecomposed silver ferricyanide. On continuing to boil the silver ferricyanide with potash, the pink precipitate again becomes black, for the potassium cyanide reduces the silver ferricyanide to ferrocyanide, which is ultimately decomposed by the silver oxide, with separation of metallic silver—

(1) $2Ag_6Fe_2Cy_{12} + 4KCN + 4H_2O = 3Ag_4FeCy_6 + K_4FeCy_6 + 2HCN + 2CO_2 + 2NH_3$;
(2) $4Ag_4FeCy_6 + 2Ag_2O = Ag_6Fe_2Cy_{12} + 12AgCy + 2FeO + Ag_2$.

In the preparation of potassium ferricyanide, if an excess of chlorine be employed, the liquid, when evaporated, deposits a precipitate of *Prussian green*, which appears to be a compound of ferric ferrocyanide and ferricyanide,

$$2Fe_4Fcy_3.Fe_2Fdcy,$$

for, when boiled with potash, it yields 5 molecules of ferric hydrate, $Fe_2(HO)_6$, 3 molecules of potassium ferrocyanide, and 1 molecule of potassium ferricyanide.

486. *Nitroprussides.*—When potassium ferricyanide is acted on by a mixture of sodium nitrite and acetic acid, it is converted into potassium nitroprusside, $K_4Fe_2Cy_{10}(NO)_2$, probably according to the equation—

$$K_6Fe_2Cy_{12} + 4HNO_2 = K_4Fe_2Cy_{10}(NO)_2 + 2HCy + H_2O + KNO_3 + KNO_2.$$

If mercuric chloride be added to the solution, mercuric cyanide crystallises out, and, on further evaporation, red prisms of sodium nitroprusside are deposited—

$$K_6Fe_2Cy_{12} + 4NaNO_2 + 2H\overline{A} + HgCl_2 =$$
$$Na_4Fe_2Cy_{10}(NO)_2 + HgCy_2 + 2KCl + 2KA + KNO_2 + KNO_3 + H_2O.$$

Sodium nitroprusside, $Na_4Fe_2Cy_{10}(NO)_2.4Aq$, is prepared by a process founded upon the above reactions (Hadow). 332 grains of potassium ferricyanide are dissolved in half a pint of boiling water, and 800 grains of acetic acid are added. Into this hot solution is poured a cold solution containing 80 grains of sodium nitrite and 164 grains of mercuric chloride in half a pint of water. The solution is kept at 60° C. for some hours, until a little no longer gives a blue coloration with ferrous sulphate (a little more sodium nitrite and acetic acid may be added if necessary). The mixture is then boiled down till it solidifies to a thick paste on cooling; this is squeezed in linen to drain off the solution of potassium acetate; the mass is dissolved in boiling water, and allowed to cool, when most of the mercuric cyanide crystallises out. On concentrating the red filtrate, and cooling, crystals of sodium nitroprusside are obtained, and may be purified by recrystallisation.

Sodium nitroprusside was originally prepared by boiling ferrocyanide with nitric acid (Playfair). Potassium ferrocyanide, in powder, is dissolved in twice its weight of strong nitric acid (1.42) mixed with an equal volume of water; effervescence takes place, from escape of CO_2 and N, and the odours of cyanogen, hydrocyanic acid, and cyanic acid may be distinguished. When the salt has dissolved, the solution is heated on a steam-bath till it no longer gives a blue with ferrous sulphate. It is then allowed to cool, when KNO_3 crystallises out, and the solution is boiled with excess of sodium carbonate and filtered; the filtrate, when evaporated, deposits crystals of nitroprusside.

Sodium nitroprusside is very soluble in water; the solution deposits a blue precipitate when exposed to light. When its solution is rendered alkaline by soda, and boiled, the NO group exerts a reducing action, ferrous hydrate being precipitated, and sodium ferrocyanide and nitrite remaining in solution. Alkaline sulphides have also a reducing effect upon the solution, producing a fugitive violet-blue colour, even in very weak solutions, rendering sodium nitroprusside a most delicate test for sulphur in organic compounds, which yield sodium sulphide when fused with sodium carbonate. The sulphur in an inch of human hair may be detected by this test. The higher (yellow) alkaline sulphides should be reduced by warming with potassium cyanide solution. Alcoholic solutions of nitroprusside and sulphide of sodium yield a purple oily compound soon decomposing into ammonia and several cyanogen compounds.

With silver nitrate, sodium nitroprusside gives a buff precipitate of *silver nitroprusside*, $Ag_4Fe_2Cy_{10}(NO)_2$, and by decomposing this with hydrochloric acid, the *hydronitroprussic acid*, $H_4Fe_2Cy_{10}(NO)_2$, may be obtained, by evaporation *in vacuo*, in red deliquescent prisms containing a molecule of water. It is very unstable.

Potassium nitroprusside may be obtained by adding potassium cyanide to ferrous sulphate, and heating the brown precipitate with potassium nitrite solution—

$$(1)\ 5KCy + 2FeSO_4 = KFe''_2Cy_5 + 2K_2SO_4;$$
$$(2)\ 2KFe''_2Cy_5 + 2KNO_2 = K_4Fe'''_2Cy_{10}(NO)_2 + 2FeO.$$

The relation between the ferrocyanide, ferricyanide, and nitroprusside may be exhibited by writing the formulæ thus—

Potassium ferrocyanide . . .	$(KCy)_2CyFe''Cy(KCy)_2$
,, ferricyanide . . .	$(KCy)_3Cy_3Fe'''_2Cy_3(KCy)_3$
,, nitroprusside* . . .	$(KCy)_2Cy_3Fe'''(NO)_2Fe'''Cy_3(KCy)_2$

487. *Chromic cyanide*, Cr_2Cy_6, is a pale green precipitate produced by KCy with chrome alum; heated with excess of KCy, it yields *potassium chromicyanide*. $K_6Cr_2Cy_{12}$, which may be obtained in yellow prisms.

Manganous cyanide, $MnCy_2$, is probably contained in the greenish precipitate by KCy in manganous acetate; an excess of KCy dissolves it to a colourless solution, from which alcohol separates blue crystals of *potassium manganocyanide*, $K_4MnCy_6.3Aq$, isomorphous with the ferrocyanide. When exposed to air, the solution of the manganocyanide absorbs oxygen, and deposits red prisms of *potassium manganicyanide*, $K_6Mn_2Cy_{12}$, isomorphous with the ferricyanide.

Cuprous cyanide, Cu_2Cy_2, is obtained as a white precipitate by boiling cupric sulphate with KCy, when *cupric cyanide*, $CuCy_2$, is first formed as a brown precipitate, which evolves cyanogen when boiled. Cuprous cyanide dissolves in KCy, and the solution yields colourless crystals of *potassium cupro-cyanide*,

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* Muller has obtained a salt having the composition $K_3Fe.CO.Cy_5$, the radical of which, *carbonyl-ferrocyanogen*, $Fe.CO.Cy_5$, corresponds to half the radical of the nitroprussides, $Fe_2(NO)_2Cy_{10}$, with CO in place of NO, but the new salt appears to be a ferrous compound.

$K_2Cu'_2Cy_4$, which gives a precipitate of *plumbic cupro-cyanide*, $PbCu_2Cy_4$, with lead acetate. By decomposing the lead salt with H_2S, a solution of the corresponding acid, $H_2Cu_2Cy_4$, is obtained, but this soon decomposes into $2HCy$ and Cu_2Cy_2.

488. *Silver cyanide*, $AgCy$, is obtained as a white precipitate when hydrocyanic acid or a cyanide is added to silver nitrate. Its insolubility in water renders its formation a very delicate test for HCy (in the absence of other acids forming insoluble silver salts) and an accurate method of estimating its quantity.

Silver cyanide is not altered by sun-light like silver chloride, and is dissolved when boiled with strong nitric acid, which does not dissolve the chloride. The nitric solution, when cooled, deposits flocculent masses of minute needles of the composition $AgCy.2AgNO_3$. Even in the cold, strong nitric acid partly decomposes the cyanide, evolving HCy, and after some hours a large quantity of it becomes converted into the above salt. The same salt is obtained by dissolving silver cyanide in a boiling strong solution of silver nitrate; it is decomposed by water, the cyanide of silver being left undissolved. It detonates when heated.

Silver cyanide, when heated, fuses, evolves cyanogen, and leaves a residue of silver mixed with *silver paracyanide*, AgC_3N_3. Silver cyanide dissolves in ammonia like the chloride, but the latter is deposited in microscopic octahedra, while the cyanide forms distinct needles; a mass of silver cyanide, moistened with ammonia and warmed, becomes converted into needles. Similar needles are obtained by boiling silver cyanide with very strong solutions of the carbonates of potassium and sodium, which dissolve the cyanide sparingly and deposit it in prismatic crystals on cooling. Potassium hydrate does not decompose silver cyanide. Potassium cyanide readily dissolves silver cyanide, forming $KAgCy_2$, which may be crystallised in six-sided tables. It is used in electro-plating.

Mercuric cyanide, $HgCy_2$, is prepared by dissolving precipitated mercuric oxide in excess of solution of hydrocyanic acid, and evaporating, when the cyanide is deposited in four-sided prisms, which dissolve in eight parts of cold water, and are insoluble in alcohol. The action of heat upon it has been mentioned at p. 604. It is one of the most stable of the cyanides, scarcely allowing the cyanogen to be detected by the ordinary tests. Dilute sulphuric and nitric acids do not decompose it, but hydrochloric acid liberates HCy. Potash and ammonia do not precipitate its solution.

Mercuric cyanide dissolves mercuric oxide when boiled, giving an alkaline solution, which deposits needles of *mercuric oxycyanide*, Hg_2OCy_2. When solutions of mercuric cyanide and silver nitrate are mixed, the solution becomes acid, and, on stirring, deposits fine needles containing $Ag.Hg.NO_3.Cy_2.2Aq$. The acid reaction of the solution proves that some of the mercuric cyanide has become converted into mercuric nitrate; the same salt may be obtained by dissolving silver cyanide in mercuric nitrate. Neither mercuric cyanide nor silver nitrate is precipitated by excess of ammonia, but a mixture of the two salts gives an abundant precipitate, containing $HgCy_2.7AgCy.2HgO$, which explodes when heated. The crystalline salt is probably $AgCy.CyHgNO_3.2Aq$, containing $HgCy_2$, in which Cy is replaced by NO_3. Other crystalline compounds of the same kind are formed by $HgCy_2$; such as $NaCy.CyHgCl$ and $KCy.CyHgI$. A potassio-mercuric cyanide, $KCy.CyHgCy.CyK$, may be obtained in fine crystals, which may be decomposed by mercuric chloride, yielding $HgCl_2.HgCy_2$ or $Hg''Cy'Cl'$.

Mercuric cyanide was originally prepared by Scheele, when he discovered that prussic acid could be prepared from Prussian blue. This was boiled with mercuric oxide and water till the blue colour had disappeared; $Fe_4(Cy_6Fe)_3 + 9HgO = 9HgCy_2 + 2Fe_2O_3 + 3FeO$. The filtered solution was mixed with sulphuric acid, shaken with iron filings, which precipitated the mercury, and distilled to obtain hydrocyanic acid; $HgCy_2 + H_2SO_4 + Fe = 2HCy + FeSO_4 + Hg$.

Mercuric cyanide may be directly obtained from potassium ferrocyanide by boiling it with mercuric sulphate (2 parts) and water (8 parts)—

$$2K_4FeCy_6 + 7HgSO_4 = 6HgCy_2 + 4K_2SO_4 + Fe_2(SO_4)_3 + Hg.$$

The mercurous cyanide is not known; when mercurous nitrate is decomposed by potassium cyanide, a solution of mercuric cyanide is formed, and metallic mercury is precipitated; $Hg_2(NO_3)_2 + 2KCy = HgCy_2 + Hg + 2KNO_3$.

Gold cyanides.—When gold-leaf is boiled with potassium cyanide in contact with air, a solution of *potassium aurocyanide* is obtained; $Au_2 + 4KCy + O + H_2O = 2KAu'Cy_2 + 2KHO$. To prepare it in larger quantity, 7 parts of gold are dissolved in a mixture of hydrochloric acid with one-fourth its volume of nitric acid, and the solution precipitated by ammonia; the *fulminating gold* so obtained is washed, and dissolved in hot water containing 6 parts of pure potassium cyanide. The filtered solution deposits colourless crystals of the aurocyanide, which are very soluble in hot water.

Aurous cyanide, AuCy, is obtained as a crystalline precipitate by adding HCl to solution of the aurocyanide of potassium.

Potassium auricyanide, $KAu'''Cy_4$, is prepared by mixing hot strong solutions of gold trichloride and potassium cyanide. It forms colourless tables, which contain a molecule of water. By decomposing it with silver nitrate, a precipitate of *silver auricyanide*, $AgAuCy_4$, is obtained, and if this be treated with HCl, avoiding excess, the silver is precipitated as AgCl, and the solution, evaporated *in vacuo,* yields crystals of *auric cyanide*, $AuCy_3.3Aq$.

Both aurocyanide and auricyanide of potassium are used in electro-gilding.

489. *Platinum cyanides.*—The cyanides of platinum have not been prepared in a pure state, but the salts known as *platinocyanides* exceed the ferrocyanides in the force with which they retain the platinum disguised to the ordinary tests for it. When potassium cyanide is strongly heated on platinum foil, the metal is attacked, and an orange-coloured mass is produced. Spongy platinum is slowly dissolved by a boiling solution of potassium cyanide, and if mixed with the solid cyanide, and heated to 600° C. in steam, the *potassium platinocyanide* is formed; $Pt + 4KCy + 2H_2O = K_2Pt''Cy_4 + 2KHO + H_2$. The platinocyanide may also be obtained by strongly heating a mixture of spongy platinum with potassium cyanide or ferrocyanide, and extracting the mass with water.

When solutions of potassium cyanide and platinic chloride are boiled together till colourless, the platinocyanide is found in solution—

$$PtCl_4 + 6KCN + 4H_2O = K_2Pt(CN)_4 + 4KCl + 2NH_3 + H_2C_2O_4.$$

Or the ammonio-platinic chloride may be boiled with potash and a strong solution of potassium cyanide until no more ammonia is evolved.

Potassium platinocyanide is also prepared by dissolving platinous chloride in solution of potassium cyanide; $PtCl_2 + 4KCy = K_2PtCy_4 + 2KCl$. It crystallises in prisms containing 3Aq, which are yellow by transmitted light, and reflect a blue colour. They are very soluble in water. The solution is colourless, and gives a characteristic blue precipitate with mercurous nitrate. Cupric sulphate also gives a blue precipitate, and if this be suspended in water and decomposed by hydric sulphide, it yields a solution of *hydroplatinocyanic acid*, H_2PtCy_4; by evaporating this, and crystallising the residue from ether, the acid is obtained in red prisms with a blue reflection, containing 5Aq, and dissolved without colour by alcohol.

Barium platinocyanide, $BaPtCy_4.4Aq$, is prepared by decomposing the cupric salt with baryta. It is dichroic, being green when looked at along the primary axis of the crystal, and yellow across it.

Magnesium platinocyanide, $MgPtCy_4.7Aq$, obtained by decomposing the barium salt with magnesium sulphate, crystallises in large prisms, which are deep red by transmitted light, but when viewed by reflected light, the sides of the prisms exhibit a brilliant beetle-green, and the ends a deep blue or purple colour. When the red salt is gently warmed, even under water, it becomes bright yellow, from production of $MgPtCy_4.6Aq$, which may be obtained in crystals from the solution at 71° C. Heated to 100° C., the yellow salt becomes white $MgPtCy_4.2Aq$, and at about 180° C. it again becomes yellow, and is then anhydrous. If a little of the yellow anhydrous salt be placed on the powdered red salt with 7Aq, it abstracts water from it, and converts it into the yellow salt with 6Aq, while it is itself changed to the white salt with 2Aq, so that a white layer is formed between two yellow layers. The yellow salt may also be obtained by crystallisation from alcohol.

When the platinocyanides are acted on, in solution, by oxidising agents, such as chlorine, bromine, and nitric acid, new salts are formed, which have a coppery lustre, and act as oxidising agents in alkaline solutions, like the ferricyanides. These were formerly called *platinicyanides*, but were shown by Hadow to contain chloro-, bromo-, &c., platinocyanides. When chlorine is passed into a hot solution of potassium platinocyanide, it deposits, on evaporation, colourless crystals of the chloroplatinocyanide, $K_2PtCy_4Cl_2.2Aq$. When these are treated with a strong solution of the platinocyanide, they are converted into copper-red needles of $5K_2PtCy_4.K_2PtCy_4Cl_2.3H_2O.18Aq$. This compound, when boiled with potash, yields the platinocyanide and potassium hypochlorite—

$$5K_2PtCy_4.K_2PtCy_4Cl_2 + 2KHO = 6K_2PtCy_4 + KClO + KCl + H_2O.$$

490. *Chlorides of cyanogen.—Liquid cyanogen chloride*, CyCl, is prepared by the action of chlorine upon moist mercuric cyanide, in the dark; $HgCy_2 + 2Cl_2 = HgCl_2 + 2CyCl$. On gently heating, the cyanogen chloride passes off in vapour, and may be condensed in a tube surrounded with a freezing mixture. It is a colourless liquid, boiling at 15°.5 C., and yielding a vapour which irritates the eyes, causing tears. When exposed to light, it becomes polymerised into the *solid cyanogen chloride*, or *cyanuric chloride*, Cy_3Cl_3, which fuses at 145° and boils at 190° C. This has also an irritating effect on the eyes. It is sparingly soluble in cold water, and is decomposed by boiling water, yielding cyanuric acid; $Cy_3Cl_3 + 3H_2O = Cy_3(HO)_3 + 3HCl$. Both the cyanogen chlorides may be obtained by the action of chlorine on hydrocyanic acid. To prepare the liquid chloride, chlorine is passed rapidly into water containing 20 per cent. of HCy, in a flask cooled in a freezing mixture and connected with a reversed condenser. The CyCl sinks to the bottom, and is distilled with mercuric oxide and calcium chloride to retain HCy and H_2O. The solid chloride is obtained by passing chlorine slowly into a solution of HCy in four parts of ether cooled in a freezing mixture; it separates as an oil, which afterwards solidifies. Cyanuric chloride may also be prepared as follows:—17 parts by weight of dry hydrocyanic acid are passed into 65 parts of chloroform kept cool by ice and salt; dry chlorine is then passed in, and continued for some time after the solution has become yellow. After standing for twelve hours, the liquid is boiled, with a reflux condenser, to expel HCl, CNCl, and Cl, after which the chloroform is distilled off, leaving the cyanuric chloride.

Cyanogen bromide, CyBr, is obtained in crystals, mixed with KBr, when bromine is gradually added to a strong well-cooled solution of KCy. On gently heating, it sublimes in crystals, which are very volatile and cause tears. When heated in a sealed tube, it becomes Cy_3Br_3.

Cyanogen iodide, CyI, is prepared by dissolving iodine in a warm strong solution of KCy, when a crystalline mass of KI and CyI is obtained on cooling, from which the CyI may be extracted by gently heating or by treatment with ether. It crystallises easily in colourless needles or tables, which are sparingly soluble in water, very volatile, and have a tear-exciting odour. Cyanogen iodide sometimes occurs in commercial iodine, and may be sublimed from it in a tube or flask plunged in boiling water.

When cyanogen iodide is heated to 100° C., in a sealed tube, with alcoholic ammonia, it yields hydriodide of guanidine—

$$CNI + 2NH_3 = CN_3H_5.HI.$$

491. *Cyanuric acid*, $Cy_3(OH)_3$, is obtained by heating urea till the melted mass solidifies again; $3CO(NH_2)_2 = 3NH_3 + (CN)_3(HO)_3$. The residue is washed with water, dissolved in potash, and the cyanuric acid precipitated by adding hydrochloric acid. A better yield is obtained by passing dry chlorine over urea kept in fusion by a gentle heat; $3CO(NH_2)_2 + Cl_3 = 2NH_4Cl + HCl + N + (CN)_3(HO)_3$. The residue is washed with cold water, and crystallised from hot water. Cyanuric acid crystallises in prisms containing 2Aq. It is insoluble in alcohol. It is a tribasic acid, forming salts in which one, two, or three atoms of the hydrogen are replaced by metal. *Trisodium cyanurate*, $(CN)_3(ONa)_3$, is insoluble in hot solution of soda, and forms a crystal-

line precipitate on heating solution of cyanuric acid mixed with excess of soda. *Barium cyanurate*, Cy_3O_3HBa, is obtained as a crystalline precipitate by dissolving cyanuric acid in ammonia, and stirring with barium chloride. It has a great tendency to deposit on the lines of friction by the stirring-rod. The most characteristic test for cyanuric acid is ammoniacal cupric sulphate, which gives a violet crystalline precipitate containing $Cy_6(OH)_4.O_2.Cu(NH_3)_2$. *Silver cyanurate*, $Cy_3(OAg)_3$, is obtained as a crystalline precipitate by adding ammonium cyanurate to silver nitrate.

Cyanic acid, CyOH, is prepared by distilling cyanuric acid (dried at 100° C.), and condensing in a receiver surrounded by a freezing mixture; $Cy_3(OH)_3 = 3CyOH$. The cyanic acid is a colourless liquid, of sp. gr. 1.14 at 0° C., which smells rather like acetic acid. It cannot be kept, for when the receiver is taken out of the freezing mixture, it becomes turbid, and presently begins to boil explosively, becoming entirely converted in a few minutes into a white hard solid, known as *cyamelide*, which appears to be polymeric with cyanic acid, and may be reconverted into it by distillation. When cyanic acid is mixed with water, heat is evolved, and the liquid becomes alkaline, from production of hydro-ammonium carbonate; $CN.OH + 2H_2O = NH_4.HCO_3$. A compound of HCl and CNOH is obtained as a fuming liquid by acting on a cyanate with dry HCl gas.

492. *Sulphocyanic acid*, CySH (*thiocyanic*), is obtained by decomposing mercuric sulphocyanate with hydric sulphide. It is a colourless pungent liquid, boiling below 100° C., being then decomposed into hydrocyanic and *persulphocyanic* acids; $3CySH = HCy + Cy_2S_3H_2$. It mixes with water, but the solution soon decomposes—

$$3CNSH + 6H_2O = CS_2 + H_2S + NH_4HCO_3 + (NH_4)_2CO_3.$$

Sulphocyanic acid and the sulphocyanates give an intense blood-red colour with ferric salts, producing ferric sulphocyanate; the red colour is bleached by mercuric chloride, which distinguishes it from ferric acetate and meconate.

Potassium sulphocyanate, or *thiocyanate*, CySK, is prepared by fusing dried potassium ferrocyanide (3 parts), potassium carbonate (1 part), and sulphur (2 parts), at a low red heat, in a clay crucible. The cooled mass is extracted by hot water, evaporated, and the residue boiled with alcohol, which deposits the sulphocyanate on cooling. KCy is formed by the reaction between the ferrocyanide and the carbonate (p. 606), and combines with the sulphur. The sulphocyanate may be obtained by direct fusion of potassium cyanide with sulphur, or by boiling sulphur with solution of the cyanide. Potassium sulphocyanate forms prismatic crystals, which are deliquescent and very soluble in water, producing great reduction of temperature. It fuses easily, becoming dark blue, and burns when heated in air, potassium sulphate being produced. When hydrochloric acid is added to a strong solution of potassium sulphocyanate, a yellow precipitate of persulphocyanic acid is obtained; this may be crystallised from hot water, and yields a yellow precipitate of *lead persulphocyanate*, $PbCy_2S_3$, with lead nitrate. When heated with sulphuric acid mixed with an equal volume of water, potassium sulphocyanate yields carbon oxysulphide, an offensive gas which burns with a blue flame; $KCNS + 2H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS$.

Perthiocyanogen, or *pseudosulphocyanogen*, $C_3N_3S_3H$, is obtained as a yellow precipitate when potassium sulphocyanate is heated with potassium chlorate and hydrochloric acid. It is used in dyeing (*canarin*).

Sodium sulphocyanate occurs in saliva. *Ammonium sulphocyanate* is prepared by acting on carbon disulphide (7 parts by weight) dissolved in alcohol (30 parts) with strong ammonia (30 parts). After standing for a day or two, with occasional shaking, until all the CS_2 has dissolved, the red solution is distilled down to one-third of its bulk, when it becomes colourless, filtered if necessary, and allowed to crystallise.

$$CS_2 + 4NH_3 = CNS.NH_4 + (NH_4)_2S.$$

It is also made on a large scale by boiling sulphur with the solution of ammonium cyanide from the gasworks. It crystallises like the potassium salt, and is very soluble in water, producing great cold. When heated, it fuses easily, and at 170° C. is metamerised into *sulpho-urea*, or *thio-carbamide*, $CS(NH_2)_2$, which crystallises easily from hot water, and resembles urea in its chemical relations.

The action of a high temperature upon ammonium sulphocyanate yields *melam*, $(C_3N_3)_2(NH_2)_4NH$; $6(CNS.NH_4) = C_6H_9N_{11} + 5H_2S + NH_4HS$. When melam is boiled with potash, it gives a base, *melamine*, $C_3N_3(NH_2)_3$, and potassium ammelide, from which acids precipitate *ammelide*, $C_3N_3.NH_2.(OH)_2$, which is insoluble in water, alcohol, and ether, and is converted into potassium cyanurate by boiling with strong potash; $C_3N_3.NH_2(OH)_2 + 2KOH = C_3N_3.OH(OK)_2 + NH_3 + H_2O$. By boiling melamine with hydrochloric acid, it is converted into *ammeline hydrochloride*; $C_3N_3(NH_2)_3 + 2HCl + H_2O = C_3N_3(NH_2)_2OH.HCl + NH_4Cl$.

The final result of the action of a high temperature upon ammonium sulphocyanate, persulphocyanic acid, perthiocyanogen, melam, melamine, and ammeline, is a light yellow insoluble body called *mellone*, $(C_3N_3)_3N_3$, which is gradually converted into cyanuric acid by boiling nitric acid. When potassium sulphocyanate is strongly heated, out of contact with air, it evolves CS_2, and leaves a residue of K_2S and *potassium mellonide*, $K_3C_9N_{13}$, which may be obtained from hot water in crystals with 3Aq. By decomposing this with $AgNO_3$, *silver mellonide*, $Ag_3C_9N_{13}$, is precipitated, and, when treated with H_2S, yields *hydromellonic acid*, $H_3C_9N_{13}$, which is decomposed by heat into ammonia and mellone.

Lead sulphocyanate, $Pb(CyS)_2$, forms a yellow crystalline precipitate when lead acetate is stirred with potassium sulphocyanide.

Silver sulphocyanate, AgCyS, is a white precipitate, very insoluble in water and in nitric acid, and sparingly soluble in ammonia.

Mercuric sulphocyanate, $Hg(CyS)_2$, is obtained as a crystalline precipitate on stirring mercuric chloride with potassium or ammonium sulphocyanate. It attracted much notice formerly as the toy called *Pharaoh's serpent*, which was a small cylinder of the sulphocyanate mixed with gum, which burnt when kindled, evolving mercury and other vapours, and swelling to a bulky vermiform mass of mellone.

Cuprous sulphocyanate, $Cu_2(CyS)_2$, precipitated by potassium sulphocyanate from a cuprous salt, is very insoluble in water and in cold dilute acids, so that copper is sometimes precipitated in this form in quantitative analysis.

493. *Cyanogen sulphide*, Cy_2S, is obtained by decomposing cyanogen iodide, dissolved in ether, with silver sulphocyanate; $CyI + AgCyS = Cy_2S + AgI$. It is a crystalline, fusible, volatile solid, soluble in alcohol and ether, but decomposed by water; potash converts it into cyanate and sulphocyanate.

Phosphorus tricyanide, Cy_3P, is sublimed in tabular crystals from a mixture of silver cyanide and phosphorus trichloride, heated in a sealed tube to 140° C. for some hours, and distilled in a current of CO_2. It inflames at a very low temperature, and is decomposed by water into hydrocyanic and phosphorous acids; $Cy_3P + 3HOH = 3CyH + P(OH)_3$.

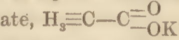
494. *Cyanides of the alcohol radicals*, or *nitriles.—Methyl cyanide*, or *acetonitrile*, $CH_3.CN$, is prepared by heating methyl iodide with potassium cyanide, or by distilling potassium sulphomethylate with potassium cyanide; $CH_3.SO_4K + KCN = CH_3.CN + KSO_4K$. It may be obtained in a purer condition by distilling acetamide with an equal bulk of P_2O_5,

which abstracts the elements of water; $C_2H_3O.NH_2 = CH_3.CN + H_2O$. The term *nitrile* was originally applied to the final product of the removal of water from a salt of ammonium, the amide being the intermediate product; it was afterwards found that the nitriles were identical with the cyanides of alcohol-radicals. Cyanogen itself is *oxalonitrile*, and may be obtained by dehydrating ammonium oxalate with P_2O_5; $(NH_4)_2C_2O_4 = (CN)_2 + 4H_2O$. Hydrocyanic acid is *formonitrile*, derivable from ammonium formate; $NH_4.CHO_2 = HCN + 2H_2O$.

Methyl cyanide is a volatile liquid of pleasant odour, boiling at 82° C. Its sp. gr. is 0.8, and it mixes with water and alcohol. The unsaturated character of the cyanogen group ($C\equiv N$) contained in it, enables it to combine with other bodies; thus, it unites with Br_2, HBr, and HI to form crystalline compounds. Certain chlorides also combine with methyl cyanide to form crystalline volatile substances which are decomposed by water; such compounds are formed with PCl_5, $SbCl_5$, and $SnCl_4$. When methyl cyanide is acted on by sodium, part of it is decomposed with violent evolution of methyl hydride, and the remainder is polymerised to form *cyanmethine*, $(CH_3)_3(CN)_3$, an organic base, soluble in water, and having a very bitter taste. It forms prismatic crystals, which may be sublimed.

By the action of atomic hydrogen (from zinc and sulphuric acid), methyl cyanide is converted into ethylamine; $CH_3.CN + H_4 = NH_2.C_2H_5$. When boiled with solution of potash, it yields ammonia and potassium acetate—

$$CH_3.CN + H_2O + KOH = NH_3 + CH_3.CO.OK.$$

This reaction is typical of the behaviour of the *alkyl cyanides*. It exhibits the characteristic disposition of the nitriles to revert to the original ammonium salts when boiled with alkalies, exactly as the amides do. It also illustrates the easy convertibility of the CN group into the CO.OH group. Moreover, it proves that *the methyl is united to the carbon and not to the nitrogen* of the CN group, so that methyl cyanide is $H_3\equiv C—C\equiv N$, the two carbon atoms remaining united in the potassium acetate,  $H_3\equiv C—C\begin{matrix}=O\\—OK\end{matrix}$.

Methyl cyanide is present, in small quantity, in coal-naphtha, and in the distillate from beet-sugar refuse.

Ethyl cyanide, or *propio-nitrile*, $C_2H_5.CN$, is obtained by methods corresponding to those which yield methyl cyanide. Ethyl iodide is heated with potassium cyanide to 180° C. for some hours. The distilled product is mixed with a weak solution of calcium chloride, when the ethyl cyanide rises to the surface and the undecomposed iodide falls to the bottom. The cyanide is rectified over fused calcium chloride to remove the water. It resembles methyl cyanide, except in being less soluble in water, and in boiling at 98° C. It combines with HCl to form a sparingly soluble crystalline compound, which absorbs water from the air, and yields propionic acid and ammonium chloride—

$$C_2H_5.CN.HCl + 2H_2O = C_2H_5.CO_2H + NH_4Cl.$$

Sodium acts on ethyl cyanide in the same way as on methyl cyanide; one part is decomposed, with evolution of butane (di-ethyl)—

$$2C_2H_5CN + Na_2 = C_4H_{10} + 2NaCN.$$

The remainder is polymerised to *cyanethine*, $(C_2H_5)_3(CN)_3$. To prepare this body, ethyl cyanide is gradually dropped on sodium, and heat applied as long as gas is evolved. The mass is washed with cold water, and dissolved in hot water, which deposits crystals of cyanethine on cooling. It is a strong monacid base. When heated with ethyl iodide, it unites with it, like a tertiary amine (p. 577), and if the iodide be treated with silver hydrate, it gives a strongly alkaline ammonium base, *ethyl-cyanethonium hydroxide*, $N_3\,C_9H_{15})'''(C_2H_5)'OH$. Strong hydrochloric acid converts cyanethine into another crystalline base, in which O'' is substituted for (N'''H')''; $N_3C_9H_{15} + HCl + H_2O = NH_4Cl + N_2C_9H_{14}O$. Phosphoric chloride replaces HO in this by Cl, yielding an unpleasant oily liquid, $N_2C_9H_{13}Cl$. When this is acted on by atomic (nascent) hydrogen, $N_2C_9H_{13}Cl + H_2 = N_2C_9H_{14} + HCl$. The compound $N_2C_9H_{14}$ is an oily volatile base with an unpleasant smell, and very poisonous, resembling in its action the natural base coniine from hemlock (p. 593). Coniine is known to be a secondary monamine, $NH.C_8H_{14}$, and the new base is probably *cyanoconiine*, $N.CN.C_8H_{14}$.

Ethyl cyanide, when boiled with potash, yields ammonia and potassium propionate; $C_2H_5.CN + KOH + H_2O = NH_3 + C_2H_5.COOK$.

Ethyl cyanide may be obtained by the action of cyanogen on zinc ethide; $2C_2N_2 + Zn(C_2H_5)_2 = Zn(CN)_2 + 2(C_2H_5.CN)$.

The cyanides of most of the other radicals of the monohydric alcohols are known, and they are the nitriles corresponding to the acid containing one more atom of carbon.

Phenyl cyanide, or *benzonitrile*, $C_6H_5.CN$, also called *cyanobenzene*, may be prepared by distilling ammonium benzoate with P_2O_5, which removes the elements of water; $C_6H_5.CO_2NH_4 = C_6H_5.CN + 2H_2O$. It is also obtained when potassium benzene sulphonate is distilled with potassium cyanide (or well-dried ferrocyanide); $C_6H_5.SO_3K + KCN = C_6H_5.CN + K_2SO_3$. It is a colourless liquid smelling of bitter almonds; sp. gr. 1.023, boiling at 191° C. When boiled with acids or alkalies, it takes up $2H_2O$ and becomes ammonium benzoate. Nascent hydrogen converts it into *benzylamine*, $C_6H_5.CH_2.NH_2$. Like other cyanides of monatomic radicals, it has a tendency to combine with hydrogen acids and haloid salts.

Benzyl cyanide, $C_7H_7.CN$, or *phenyl-aceto-nitrile*, is obtained by heating benzyl chloride with potassium cyanide and alcohol. It occurs in the essential oils of nasturtium and cress. When boiled with alkalies, it yields ammonia and *phenyl acetic* (or *a-toluic*) *acid*, $CH_2.C_6H_5.CO_2H$.

495. *Isocyanides*, or *carbamines*.—It has been seen that the cyanides of ethyl and methyl may be obtained by heating their iodides with potassium cyanide. If silver cyanide be substituted for potassium cyanide, there are obtained two liquids of unpleasant odour which have lower boiling points than the cyanides; they have the same composition as these, and are therefore called isocyanides. They are much less easily acted on by alkalies than the cyanides, and, when heated with acids, they yield formic acid and an amine which contains the radical of the isocyanide; thus methyl isocyanide, heated with aqueous hydrochloric acid, gives formic acid, HCO_2H, and methylamine, $H_3C.NH_2$. This shows that *the methyl is united to the nitrogen and not to the carbon* of the CN group, and that methyl isocyanide is $H_3{\equiv}C{-}N{\equiv}C$, and its decomposition by aqueous acids would be expressed by the equation—

$$CH_3.NC + 2H_2O = CH_3.NH_2 + CO_2H_2.$$

The term *carbamine* refers to the idea formerly entertained that the isocyanides were *amines* in which carbon is substituted for hydrogen; thus, methyl carbamine, $NC.CH_3$, might be regarded as methylamine, NH_2CH_3, in which C'' is substituted for H_2. The isocyanides often accompany the cyanides of the alcohol-radicals, especially when prepared by distilling the acid ethereal salts, such as potassium sulphethylate with potassium cyanide. For this reason the cyanides of alcohol-radicals were formerly described as having an offensive smell, which is really characteristic of the isocyanides mixed with them.

Methyl isocyanide, or *methyl carbamine*, $H_3C.NC$, is prepared by heating methyl iodide with silver cyanide and ether, in a sealed tube, to 140° C., when a crystalline compound of the isocyanides of methyl and silver is formed—

$$H_3C.I + 2AgCN = (H_3C.NC)(AgNC) + AgI.$$

This is distilled with water and potassium cyanide, when the methyl isocyanide passes over. It is lighter than water (sp. gr. 0.76) and moderately soluble in it. It has an extremely unwholesome smell, and boils at 58° C. Methyl carbamine is slightly alkaline; it combines with HCl gas, forming a crystalline hydrochloride, which is decomposed by water into formic acid and methylamine hydrochloride; $H_3C.NC.HCl + 2H_2O = H_3C.NH_2.HCl + HCO_2H$.

Ethyl isocyanide, or *ethyl carbamine*, $H_5C_2.NC$, may be prepared in the same way as the methyl compound. It may also be obtained by distilling an alcoholic solution of ethylamine with chloroform and solid potash—

$$H_5C_2.NH_2 + HCCl_3 + 3KOH = H_5C_2.NC + 3KCl + 3HOH.$$

The ethyl carbamine is obtained from the distillate by fractional distillation. It boils at 79° C., and has a repulsive odour like hemlock. It is lighter than water, and slightly alkaline. When heated with water to 180° C. for some hours, it is converted into ethylamine formate; $H_5C_2.NC + 2H_2O = H_5C_2.NH_2.HCO_2H$. Heated alone, in a sealed tube, to 180° C., it is metamerised into propionitrile; $H_5C_2.NC = H_5C_2.CN$. Ethyl carbamine combines readily with HCl, and forms a crystalline salt. Aqueous acids convert it into formic acid and ethylamine. If the hydrochloride be treated with very strong potash, well cooled, an oily layer of *ethyl formamide* separates on the surface; $H_5C_2.NC + H_2O = H_5C_2.NH_2CO$. Glacial acetic acid also converts ethyl carbamine into ethyl formamide, with great evolution of heat and production of acetic anhydride—

$$H_5C_2.NC + 2(C_2H_3O.OH) = H_5C_2.NH_2CO + (C_2H_3O)_2O.$$

Phenyl isocyanide, or *phenyl carbamine*, $H_5C_6.NC$, is prepared by mixing aniline with a saturated alcoholic solution of potash, and gradually adding chloroform; the distillate is treated with oxalic acid to remove aniline, with potash to remove water, and re-distilled. Phenyl carbamine has a very terrible odour; it is green by transmitted light, and shows a blue reflection. It begins to boil at 167° C., but soon decomposes, being converted, at 230° C., into an odourless liquid which crystallises on cooling. When heated, in a sealed tube, to 200° C., phenyl carbamine slowly metamerises into phenyl cyanide, or benzonitrile, $H_5C_6.CN$. Treated with acids, it yields formic acid and salts of phenylamine (aniline); $H_5C_6.NC + 2H_2O = H_5C_6.NH_2 + HCO_2H$.

The examples above given show that *an amine may be converted into a carbamine by treatment with chloroform and potash.*

496. *Potassium cyanate*, KO.CN, is prepared by passing gaseous cyanogen chloride into solution of potash, well cooled—

$$Cl.CN + 2KOH = KO.CN + KCl + H_2O.$$

It crystallises in needles, which fuse when heated, and become metamerised into the isocyanate.

Potassium isocyanate, or *pseudocyanate*, K.NC.O, formerly called potassium cyanate, is formed when the cyanide is oxidised by fusion in contact with air or with metallic oxides. It may be prepared by oxidising potassium ferrocyanide with potassium dichromate. Four parts of perfectly dried ferrocyanide are intimately mixed with 3 parts of potassium dichromate; the mixture is thrown, in small portions, into a porcelain or iron dish, heated sufficiently to kindle it. When the whole has smouldered and blackened, it is allowed to cool, introduced into a flask, boiled with strong alcohol, and filtered hot; the isocyanate crystallises out on cooling, and the mother-liquor may be employed to extract a fresh portion. Potassium isocyanate crystallises in plates; it is decomposed by moist air into hydropotassium carbonate and ammonia; $K.NC.O + 2H_2O = KHCO_3 + NH_3$. It is very soluble in water, but the solution soon decomposes, especially if heated, into potassium and ammonium; carbonates $2(K.NC.O) + 4H_2O = CO(OK)_2 + CO(ONH_4)_2$. If the freshly prepared solution be mixed with dilute acetic acid, a crystalline precipitate of dihydropotassium cyanurate is obtained; $3KNCO + 2HOC_2H_3O = KH_2C_3N_3O_3 + 2KOC_2H_3O$. Solution of potassium isocyanate effervesces with sulphuric and hydrochloric acids, evolving carbon dioxide, together with some pungent vapour of cyanic (or isocyanic) acid, and leaving ammonium sulphate or chloride in solution.

Ammonium cyanate, $NH_4.O.CN$, is prepared by mixing vapour of cyanic acid with ammonia gas in excess, when it is deposited in minute crystals, which effervesce with acids, evolving CO_2. If the cyanate is kept for some time, or if its aqueous solution be boiled, it no longer effervesces with acids nor evolves ammonia with cold potash, having become metamerised into urea, $(NH_2)_2CO$, having probably first changed into the isocyanate.

Ammonium isocyanate, $NH_4.NC.O$, is formed when potassium isocyanate is decomposed by ammonium sulphate. By employing strong solutions and cooling artificially, the bulk of the potassium sulphate may be crystallised out. The isocyanate has not been crystallised, for, when its solution is evaporated, it metamerises into urea; $NH_4.NC.O = (NH_2)_2CO$. By evaporating the solution to dryness on a steam-bath, and treating with strong alcohol, the potassium sulphate is left undissolved, and urea may be obtained in crystals from the solution. As a class experiment, a strong solution of potassium (iso)cyanate may be mixed with an equal volume of a strong solution of ammonium sulphate, and divided into two parts, one of which is boiled for a minute, and cooled. If both portions be now stirred with strong (colourless) nitric acid, the first will simply effervesce violently, but the second will deposit abundant crystals of urea nitrate.

Artificial urea.—The preparation of urea without having recourse to urine attracted much attention as one of the earliest examples of the artificial formation of an animal product from mineral sources. The original process (Liebig and Wöhler) was the following :—56 parts of well-dried potassium ferrocyanide are mixed with 28 parts of dried manganese di-oxide, the mixture heated to dull redness in an iron dish, and stirred until it ceases to smoulder. The cooled residue is treated with cold water, filtered, and the solution (of potassium (iso)cyanate) decomposed with 41 parts of crystallised ammonium sulphate. It is then evaporated to dryness on a steam-bath, and treated with strong alcohol to extract the urea. Urea has been described at p. 590.

Cyanamide, $H_2N.CN$, may be obtained by fusing urea with sodium—

$$(NH_2)_2CO + Na = H_2N.CN + NaOH + H.$$

The mass is dissolved in water, ammonia added in excess, and silver nitrate, which gives a yellow precipitate of $Ag_2N.CN$; this is washed, dried, covered with ether, and decomposed by H_2S, when Ag_2S and $H_2N.CN$ are produced, the latter dissolving in the ether, from which it may be crystallised.

Cyanamide may also be prepared, like other amides, by acting on ammonia, dissolved in ether, with gaseous cyanogen chloride—

$$2NH_3 + CN.Cl = H_2N.CN + NH_4Cl.$$

Another reaction which furnishes it is that between sulpho-urea (p. 617) and mercuric oxide ; $(NH_2)_2CS + HgO = H_2N.CN + HgS + H_2O$. Cyanamide forms crystals soluble in water, alcohol, and ether. HCl passed into its ethereal solution, gives crystals of $H_2N.CN.2HCl$. Nitric acid converts it into urea nitrate—

$$H_2N.CN + H_2O + HNO_3 = H_2N.CO.NH_2.HNO_3.$$

When heated, cyanamide fuses at 40° C., and is converted into *melamine*, or *cyanuramide*, $(H_2N)_3(CN)_3$, with evolution of much heat.

497. GUANIDINE, or *carbon-diamide-imide*, $C(NH_2)_2(NH)''$, formerly called *carbotriamine*, $(N_3H_5C^{iv})$, is prepared by heating ammonium sulphocyanate in a retort to 190° C. for several hours. Sulpho-urea is first produced by metameric change, and is converted into cyanamide ; $(NH_2)_2CS = H_2N.CN + H_2S$; the cyanamide then acts upon the remaining ammonium sulphocyanate, and converts it into guanidine sulphocyanate ; $H_2N.CN + NH_4.S.CN = C(NH_2)_2NH.HSCN$. This is dissolved in a little water, mixed with half its weight of potassium carbonate, and evaporated to dryness, when a mixture of guanidine

carbonate and potassium sulphocyanate is obtained. This is boiled with alcohol, which dissolves the sulphocyanate, and leaves *guanidine carbonate*, $(N_3H_5C)_2.H_2CO_3$, which may be recrystallised from water. This is converted into *guanidine sulphate*, $(N_3H_5C)_2.H_2SO_4$, and decomposed by baryta-water; the filtrate from the $BaSO_4$ is evaporated over sulphuric acid, when guanidine is obtained as a deliquescent crystalline substance, which is strongly alkaline, and absorbs CO_2 from the air. It is a strong monacid base, and yields well-crystallised salts.

Guanidine nitrate, $N_3H_5C.HNO_3$, like urea nitrate, is sparingly soluble in water, and crystallises in plates. Guanidine is soluble in alcohol. Its platinum salt, $2N_3H_6CCl.PtCl_4$, is sparingly dissolved by absolute alcohol. When heated with baryta-water, guanidine undergoes hydrolysis, yielding urea and ammonia; $C(NH_2)_2NH + H_2O = (NH_2)_2CO + NH_3$. Heated with strong potash, it gives potassium carbonate and ammonia—

$$C(NH_2)_2(NH)'' + 2KOH + H_2O = C(OK)_2O + 3NH_3.$$

Dilute sulphuric acid, when heated, converts it into ammonia and urea, which combine with the acid.

Guanidine was so called because originally obtained by the oxidising action of potassium chlorate and HCl on *guanine*, a feeble base extracted from guano. Guanidine has not received any practical application, but is of great theoretical interest as an amide-imide compound, formed upon the CH_4 type by the replacement of H_2 by two $(NH_2)'$ groups, and of the remaining H_2 by the imidogen group $(NH)''$. When guanidine exchanges this NH group for O'', it is converted into urea.

Synthesis of guanidine.—Being a mono-carbon compound, guanidine is easily obtained synthetically. Cyanogen iodide is converted into guanidine hydriodide by heating with ammonia dissolved in alcohol, in a sealed tube, at 100° C.; $I.CN + 2NH_3 = C(NH_2)_2NH.HI$. Guanidine hydrochloride is formed by heating cyanamide, dissolved in alcohol, with ammonium chloride to 100° C. in a sealed tube—

$$H_2N.CN + NH_3.HCl = C(NH_2)_2NH.HCl.$$

This illustrates a *general reaction for converting an amine into a guanidine by heating the hydrochloride of the amine with cyanamide dissolved in alcohol.*

Ethyl orthocarbonate (p. 559) reacts with ammonia to form guanidine; $C(OC_2H_5)_4 + 3NH_3 = C(NH_2)_2(NH)'' + 4HOC_2H_5$.

Chloropicrin also yields guanidine when heated to 100° C. with alcoholic ammonia; $CNO_2Cl_3 + 7NH_3 = C(NH_2)_2(NH)'' + 3NH_4Cl + NH_4NO_2$.

Diphenyl guanidine, or *melaniline*, $C(N.H.C_6H_5)_2NH$, is a crystalline base produced by the action of cyanogen chloride on aniline—

$$Cl.CN + 2NH_2C_6H_5 = C(NH.C_6H_5)_2NH.HCl.$$

498. *Dicyanimide*, $HN(CN)_2$, is produced by the action of potash on solution of potassium cyanate; $3KOCN + H_2O = (KO)_2CO + KHO + HN(CN)_2$. On neutralising the solution with nitric acid and adding silver nitrate, a precipitate of $AgN(CN)_2$ is obtained. Potassium isocyanate, K.NCO, does not yield dicyanimide.

Methyl cyanate, $H_3C.O.CN$, is prepared by passing gaseous cyanogen chloride into a well-cooled alcoholic solution of sodium methylate; $Cl.CN + H_3C.O.Na = ClNa + H_3C.O.CN$. It is left, after distilling off the alcohol, as a liquid which soon polymerises to a crystalline mass of *methyl cyanurate*, $(H_3C)_3O_3(CN)_3$.

Ethyl cyanate (*cyanetholin*), $H_5C_2.O.CN$, is obtained in a similar way, and also polymerises easily. When distilled with potash, it yields alcohol and potassium cyanurate; $3(H_5C_2.O.CN) + 3KOH = 3(H_5C_2.OH) + K_3O_3(CN)_3$.

499. *Methyl isocyanate*, or *methyl carbimide*, $H_3C.NC.O$, was formerly regarded as the normal cyanate, being obtained by distilling potassium sulphomethylate with potassium cyanate; $KCH_3SO_4 + K.O.CN = H_3C.NC.O + K_2SO_4$. It is also obtained by oxidising methyl isocyanide with mercuric oxide; $H_3C.NC + HgO = H_3C.NC.O + Hg$. It is a volatile liquid with a suffocating odour. When distilled with potash, it yields methylamine, showing that the methyl is attached to the nitrogen; $H_3C.N.CO + 2KOH = H_3C.NH_2 + CO(OK)_2$. Ammonia gas converts methyl isocyanate into *methyl urea* ($H_3C.NC.O + NH_3 = NH_2.NHCH_3.CO$) resembling urea itself.

Dimethyl urea, $(NH.CH_3)_2CO$, is formed by the action of water on methyl isocyanate; $2(H_3C.NC.O) + H_2O = (NH.CH_3)_2CO + CO_2$.

Ethyl isocyanate, or *ethyl carbimide*, $H_5C_2.NC.O$, is prepared like the methyl compound, which it resembles. Its sp. gr. is 0.9, and it boils at 60° C. It yields ethylamine when distilled with potash, and triethylamine with sodium ethylate; $H_5C_2.NC.O + 2(C_2H_5.ONa) = (H_5C_2)_3N + CO(ONa)_2$.

Ethyl urea, $NH_2.NHC_2H_5.CO$, *diethyl urea*, $(NHC_2H_5)_2CO$, and *triethyl urea*, $NHC_2H_5.N(C_2H_5)_2.CO$, have been obtained.

Methyl-ethyl urea, $NHCH_3.NHC_2H_5.CO$, is formed by the action of methylamine on ethyl isocyanate; $H_5C_2.NC.O + NH_2CH_3 = NHCH_3.NHC_2H_5.CO$.

500. *Allyl isosulphocyanate*, $H_5C_3.NCS$, is the *essential oil of mustard*, obtained by grinding black mustard seeds with water, and distilling. It does not exist in the seed, but is produced by the decomposition of *potassium myronate* contained in the seed, induced by a peculiar ferment called *myrosin*, which causes the myronate to split up into the essence of mustard, glucose, and hydropotassium sulphate; $KC_{10}H_{18}NS_2O_{10} = H_5C_3.NCS + C_6H_{12}O_6 + KHSO_4$. The seed yields about 0.5 per cent. of the oil.

The potassium myronate may be obtained from ground mustard by rendering the myrosin inactive by boiling alcohol, and then extracting with cold water, which dissolves the myronate. The solution is evaporated to a small bulk and mixed with alcohol, which precipitates the potassium myronate. The free acid is not known, being very unstable.

Myrosin is prepared by extracting ground white mustard with cold water, evaporating the filtrate to a syrup below 40° C., and adding alcohol in small quantity, when the myrosin is precipitated. It is a body somewhat resembling albumen, being coagulated and rendered inactive by heat. Its aqueous solution, when added to potassium myronate, causes it in a few minutes to smell of mustard and become acid; it also becomes turbid from the separation of small globular cells like those of yeast. Myrosin occurs in other plants than mustard, such as the radish, rape, cabbage, and swede, all belonging to the same natural order as mustard (*Cruciferæ*). Mignonette root also furnishes mustard oil.

Essential oil of mustard has sp. gr. 1.017, and boils at 150° C. It is insoluble in water, but dissolves in alcohol and ether. It is the cause of the pungent odour of mustard paste and of its power to redden and irritate the skin. It is slowly decomposed by light, depositing a yellow precipitate. When heated with water to 100° C. for some time, it loses sulphur and becomes *crotono-nitrile*, $C_3H_5.CN$, which is present in considerable quantity in commercial mustard oil. When mustard oil dissolved in alcohol is acted on by HCl and Zn, it yields allylamine; $H_5C_3.NCS + H_4 = H_5C_3.NH_2 + CH_2S$ (*formic thio-aldehyd*). By mixing mustard oil with ammonia and passing ammonia gas, *allyl-thio-urea*, or *thio-sinnamine*, $NH_2.NH(C_3H_5).CS$, is obtained, forming prismatic crystals soluble in water, alcohol, and ether, and having a bitter taste. It is a weak base. When heated with lead hydrate, it loses H_2S, and becomes *allyl cyanamide*, $NHC_3H_5.CN$, which afterwards polymerises into *sinnamine*, or *tri-allyl melamine*, $(NHC_3H_5)_3(CN)_3$. This is a strongly alkaline base.

If allyl bromide be decomposed by ammonium sulphocyanate, at a low temperature, *allyl sulphocyanate*, $H_5C_3.SCN$, is formed, which has no smell of mustard. When this is heated, it boils at 161° C., but the boiling point soon falls, and a strong smell of mustard is perceived. When the boiling point has reached 149° C., the whole distils over as allyl isosulphocyanate, $H_5C_3.NCS$, or mustard oil. Allyl sulphocyanate, decomposed by potash, yields potassium sulphocyanate and allyl alcohol; $H_5C_3.SCN + KOH = H_5C_3.OH + K.SCN$; allyl isosulphocyanate gives allylamine; $H_5C_3.NCS + 4KOH = H_5C_3.NH_2 + K_2S + CO(OK)_2 + H_2O$.

Mustard oil is also obtained artificially by distilling allyl iodide (p. 554) with potassium sulphocyanate; $C_3H_5I + KSCN = C_3H_5.NCS + KI$. When *ethyl* iodide is treated in the same way, ethyl sulphocyanate, $C_2H_5.SCN$, is obtained. To obtain the *ethyl isosulphocyanate*, or *ethyl mustard oil*, or *ethyl thiocarbimide*, $C_2H_5.NCS$, ethylamine dissolved in alcohol is digested with carbon disulphide, distilled nearly to dryness, and the residue in the retort boiled with solution of mercuric chloride. All primary amines yield the corresponding mustard oils when treated in this manner, and, since the odour is quite characteristic, the treatment with carbon disulphide and mercuric chloride is known as the *mustard-oil test for primary bases.*

The mustard-oil reaction is easily explained. It will be remembered that, when CO_2 is dissolved in water, the solution is supposed to contain carbonic acid, $CO(OH)_2$. When CO_2 is combined with dry ammonia, *ammonium carbamate* is formed; carbamic acid being $CO.OH.NH_2$, the reaction is—

$$CO_2 \quad + \quad 2NH_3 \quad = \quad CO.ONH_4.NH_2.$$

If CS_2 be substituted for CO_2 (the CS_2 employed in alcoholic solution), *ammonium sulphocarbamate* is produced; $CS_2 + 2NH_3 = CS.SNH_4.NH_2$. When ethylamine is used instead of ammonia, the product is *ethyl-ammonium ethyl-sulphocarbamate;* $CS_2 + 2NH_2(C_2H_5) = CS.SNH_3(C_2H_5)NH(C_2H_5)$. On decomposing this with mercuric chloride, it yields the corresponding mercuric salt, which is decomposed, by boiling with water, into ethyl isosulphocyanate, mercuric sulphide, and hydric sulphide; $Hg(CS.S.NHC_2H_5)_2 = HgS + H_2S + 2C_2H_5NCS$.

When mustard oil is heated with potassium sulphide, it yields *di-allyl sulphide*, $(C_3H_5)_2S$, which is the *essential oil of garlic.*

Butyl isosulphocyanate, $C_4H_9.NCS$, is the *essential oil of scurvy-grass*, another cruciferous plant, and is sometimes sold as mustard oil, but it has a higher boiling point, 160° C.

Potassium isosulphocyanate, K.NCS, is obtained by heating persulphocyanic acid (p. 616) with alcoholic solution of potash. It forms crystals which are soluble in water; the solution does not give the red sulphocyanate reaction with ferric salts. It is converted into normal sulphocyanate by boiling or fusing.

501. *Carbamides, carbimides, sulpho-* or *thio-carbamides*, and *sulpho-* or *thio-carbimides.*—The termination *-amide* originally implied the presence of the *amidogen* group, $(NH_2)'$, and the termination *-imide* denoted the presence of the *imidogen* group, $(NH)''$. *Urea* was called *carbamide* because its formula, $CO(NH_2)_2$, shows it to be derivable from ammonium carbonate, $CO(ONH_4)_2$, by the loss of $2H_2O$ (see p. 586). *Sulpho-urea*, or *thio-urea*, $CS(NH_2)_2$, was then called *sulphocarbamide* or *thiocarbamide. Cyanic acid* was called *carbimide* because its formula, CO.NH, shows that it differs from urea in containing the NH group instead of the two NH_2 groups. *Sulphocarbimide*, or *thiocarbimide*, CS.NH, has not been isolated, but it is evidently carbimide in which the oxygen is replaced by sulphur. When it was found that there were two compounds having the composition of potassium cyanate, viz., the *normal cyanate*, KO.CN, and the *isocyanate*, K.NCO, or CO.NK, the name *carbimide* was reserved for the (as yet unknown) *isocyanic acid*, H.NCO, or CO.NH. *Sulphocarbimide*, or *thiocarbimide*, now denotes *isosulphocyanic acid*, H.NCS, or CSNH.

Hence the *isocyanates* are now termed *carbimides*, and the *isosulphocyanates* or *isothiocyanates* are called *sulphocarbimides* or *thiocarbimides.*

In the subjoined comparison of formulæ, R′ represents any monad radical exchangeable for H.

Carbamides or Ureas.	Sulphocarbamides or Thio-ureas.	Carbimides or Iso-cyanates.	Sulphocarbimides or Iso-thio-cyanates.
$CO(NR'_2)_2$	$CS(NR'_2)_2$	$R'.NCO$	$R'.NCS$

502. *Appendix to the cyanogen compounds.*—*Chrysean*, $C_4H_5S_2N_3$, is obtained by covering potassium cyanide with water, in a flask, and saturating with H_2S gas; $4KCN + 5H_2S = C_4H_5S_2N_3 + 2K_2S + NH_4HS$. It crystallises from boiling water in golden needles, soluble in alcohol, ether, acids, and alkalies. Its alcoholic solution is red, and changes to a fugitive green on adding a little alkali. It may possibly have the formula $(CN)'_3(HS)'_2(CH_3)'$.

503. *Fulminates.*—The salts known as fulminates are prepared from the fulminates of mercury and silver, obtained when those metals are treated with nitric acid and alcohol.

Mercuric fulminate, $Hg''\left\{\begin{matrix}O.CN\\ .CN\end{matrix}\right\}O$, is prepared on a small scale, with safety, by carefully observing the following directions:—Dissolve 25 grs. (or 1.6 grm.) of mercury in half a measured ounce (or 14 c.c.) of ordinary concentrated nitric acid (sp. gr. 1.42) in a half-pint beaker, covered with a dial-glass; the solution may be allowed to take place in the cold, or it may be accelerated by gently heating. The solution contains mercuric nitrate, nitric acid, and nitrous acid. When all the mercury is dissolved, remove the beaker to a distance from any flame, and pour into it, at arm's length, 5 measured drachms (17.5 c.c.) of alcohol (sp. gr. 0.87). Very brisk action soon begins, and the fulminate separates as a crystalline precipitate; dense white fumes pour over the sides of the beaker, having the odours of nitrous ether and aldehyd; they also contain mercury compounds and hydrocyanic acid, and are very poisonous. When red fumes begin to appear abundantly, some water is poured in to stop the action (which occupies only two or three minutes), and the fulminate is collected on a filter, washed with water as long as the washings taste acid, and dried by exposure to air.

On a large scale the preparation is carried out under sheds. At Montreuil, 300 grammes of mercury are dissolved in 3 kilogrammes of colourless nitric acid, of sp. gr. 1.4, in the cold. The solution is transferred to a retort, and 2 litres of strong alcohol are added. In summer no heat is required, and the vapours are condensed in a receiver and added to a fresh charge. When the action has ceased, the contents of the retort are poured into a shallow pan, and, when cold, the fulminate is collected in a conical earthen vessel partially plugged at the narrow end. It is washed with rain-water, and drained until it contains 20 per cent. of water, being stored in that state.

Mercuric fulminate, thus prepared, has a grey colour from the presence of finely divided mercury, and sometimes contains mercuric oxalate. It may be purified by dissolving it in 100 parts of boiling water, which leaves the metal and the oxalate undissolved, and deposits the fulminate on cooling in lustrous white prisms. It should not be kept in a stoppered bottle, as it would easily detonate by friction between the stopper and the neck of the bottle. The blow of a hammer causes it to detonate sharply with a bright flash and grey fumes of mercury: $HgC_2N_2O_2 = Hg + 2CO + N_2$. It is also detonated by being touched with a wire heated to 195° C., or by an electric spark, or by contact with strong sulphuric or nitric acid. Its sp. gr. being 4.4, a small volume of it evolves a large volume of gas; according to the above equation, the gas and vapour would occupy more than 1340 times the volume of the solid, at the ordinary temperature, and the volume at the moment of detonation would be much greater, because the fulminate evolves 403 units of heat (per unit) in its decomposition, and this would expand the evolved gases and greatly increase their mechanical effect. It is estimated that a pressure of 48,000 atmospheres is thus produced.

The explosive nature of the fulminate is due to its containing an oxidising group (Hg linked to O) and a cyanide group (Hg linked to CN), for, as is well known, the cyanides (*e.g.*, KCy) form explosive mixtures with oxidising agents (*e.g.*, KNO_3 and $KClO_3$).

The formation of mercuric fulminate has not been clearly explained; when nitric acid acts on alcohol, several products are obtained, among which are nitrous acid, arising from the reduction of nitric acid, and some hydrocyanic acid. The formation of the cyanogen group may be explained by the tendency of nitrous acid to substitute N for H_3 in organic compounds, and it might be expected that the action of nitrous acid on alcohol would be—

$$CH_3.CH_2HO + 2HNO_2 = CN.CN.O + 4H_2O;$$

but the group $(CN)_2O$ appears to be too unstable to exist separately; the same is the case with the corresponding hydrate, $(CN)_2(OH)_2$; but it has been seen that mercury and silver much increase the stability of cyanogen compounds, so that by substituting Hg'' or Ag_2 for the H_2 in the above formula, a more stable body is produced. The production of mercuric fulminate by the action of nitrous acid (formed by the reduction of nitric acid by mercury or alcohol) and mercuric nitrate upon alcohol may be plausibly expressed by the equation—

$$CH_3.CH_2HO + 2HNO_2 + Hg''O_2(NO_2)_2 = CN.CN(Hg''O_2)'' + 3H_2O + 2(HO.NO_2).$$

The formula $(CN)_2(OH)_2$ represents the hypothetical *fulminic acid*, which would stand between cyanic acid, CN.OH, and cyanuric acid, $(CN)_3(OH)_3$.

When mercuric fulminate is dissolved in strong hydrochloric acid, it yields mercuric chloride, formic acid, and hydroxylamine hydrochloride (or hydroxylammonium chloride). The reaction may be represented in two equations, the first representing the formation of the mercuric chloride and unstable fulminic acid, $HgO_2(CN)_2 + 2HCl = (HO)_2(CN)_2 + HgCl_2$. The fulminic acid then reacts with water, exchanging its N''' for $H'O''$, and becoming formic acid—

$$\begin{matrix} H.O.CN \\ H.CN.O \end{matrix} + 4HOH = \begin{matrix} H.O.CHO \\ HO.CHO \end{matrix} + 2NH_2(OH)'.$$

If the mercury be precipitated as sulphide by H_2S, and the filtered solution evaporated, the hydroxylamine hydrochloride will be left. This is the best process for preparing that salt. If dilute hydrochloric acid be employed, hydrocyanic acid and carbonic acid are produced together with hydroxylamine—

$$(CN)_2(OH)_2 + 2HOH = CO(OH)_2 + CN.H + NH_2(OH).$$

When decomposed by hydric sulphide, mercuric fulminate yields sulphocyanic acid, ammonia, carbon dioxide, and sulphur, which forms HgS. Boiled with dilute sulphuric acid, it yields mercurous sulphate, formic acid, and carbon dioxide.

Bromine acts on mercuric fulminate, producing mercuric bromide and the compound $Br_2CN.O.NCO$, isomeric with dibromonitroacetonitrile, $Br_2.NO_2.C.CN$ (acetonitrile, or methyl cyanide, $H_3C.CN$). This formerly induced the belief that mercuric fulminate was the mercury nitroacetonitrile, $HgNO_2C.CN$. When excess of bromine acts upon mercuric fulminate, in an alkaline solution, it yields cyanogen bromide and bromopicrin or nitrobromoform; the action may be represented in two stages—

$$(1)\quad HgO(CN)_2O + 2Br_2 = HgBr_2 + Br_2CN.O.NCO;$$

$$(2)\quad Br_2CN.O.NCO + Br_2 = BrCN + Br_3C.NO_2 \text{ (nitrobromoform).}$$

Chlorine acts in a similar manner, producing chloropicrin, or nitrochloroform, $(Cl_3C.NO_2)$. As these bodies are derivatives of methane, $(H_3C.H)$, it was at one time believed that mercuric fulminate had the constitution $Hg''(CN)'(NO_2)'C^{iv}$.

Cap composition.—The explosion of mercuric fulminate is so violent and rapid that it is necessary to moderate it for percussion caps. For this purpose it is mixed with potassium nitrate or chlorate, the oxidising property of these salts possibly causing them to be preferred to any merely inactive substances, since it would tend to increase the temperature of the flash by burning the carbonic oxide into carbon dioxide, and would thus insure the ignition of the cartridge. The military caps, in this country, potassium chlorate is always mixed with the fulminate, and powdered glass is sometimes added to increase the sensibility of the mixture to explosion by percussion. Antimony sulphide is sometimes substituted for powdered glass, apparently for the purpose of lengthening the flash by taking advantage of the powerful oxidising action of potassium chlorate upon that compound (p. 164). Since the composition is very liable to explode under friction, it is made in small quantities at a time, and without contact with any hard substance. After a little of the composition has been introduced into the cap, it is made to adhere and waterproofed by a drop of solution of shell-lac in spirit of wine.

If a thin train of mercuric fulminate be laid upon a plate, and covered, except a little at one end, with gunpowder, it will be found, on touching the fulminate with a hot wire, that its explosion scatters the gunpowder, but does not inflame it. On repeating the experiment with a mixture of 10 grains of the fulminate and 15 grains of potassium chlorate, made upon paper with a card, the explosion will be found to inflame the gunpowder.

By sprinkling a thin layer of the fulminate upon a glass plate, and firing it with a hot wire, the separated mercury may be made to coat the glass, so as to give it all the appearance of a looking-glass.

Although the effect produced by the explosion of mercuric fulminate is very violent in its immediate neighbourhood, it is very slightly felt at a distance, and the sudden expansion of the gas will burst fire-arms, because it does not allow time for overcoming the inertia of the ball, though, if the barrel escape destruction, the projectile effect of the fulminate is found inferior to that of powder. It has been proved by experiment that the mean pressure exerted by the explosion of mercuric fulminate is very much lower than that produced by gun-cotton, and only three-fourths of that produced by nitroglycerin. Its great pressure is due to its instantaneous decomposition into CO, N, and Hg vapour within a space not sensibly greater than the volume of the fulminate itself, which volume being very small, on account of the high density of the fulminate, the escaping gases exert an enormous pressure at the moment of explosion. This detonating property of mercuric fulminate renders it exceedingly useful for effecting the detonation of gun-cotton and nitroglycerin. Berthelot finds that even such stable gases as acetylene, cyanogen, and nitric oxide are decomposed into their elements by the detonation of mercuric fulminate.

504. *Silver fulminate*, $\left.\begin{matrix}\mathrm{AgO.CN}\\ \mathrm{Ag.CN}\end{matrix}\right\}\mathrm{O}$, is prepared in a similar way to the mercury salt. Ten grains (or 0.65 grm.) of silver are dissolved, by gently heating, in 70 minims (or 5 c.c.) of ordinary strong nitric acid (sp. gr. 1.42) and 50 minims (or 3.5 c.c.) of water. As soon as the silver is dissolved, the lamp is removed, and 200 minims (or 14 c.c.) of alcohol (sp. gr. 0.87) are added. If the action does not commence shortly, a very gentle heat may be applied until effervescence begins, when the fulminate will be deposited in fine needles, and may be further treated like the mercuric salt. In some cases a little red nitric acid is necessary to start the action. The copper in silver coin does not interfere with the preparation of the fulminate. It may also be obtained as a crystalline precipitate by warming solution of silver nitrate with nitric acid and alcohol until effervescence begins.

Silver fulminate is far more dangerous than mercuric fulminate, and, if stored dry, should be wrapped up, in small portions, in paper. Even if wet, it is not safe in a glass bottle. When dry, it should be lifted with a slip of card.

Silver fulminate crystallises in shining prisms, and is more soluble in boiling water (36 parts) than mercuric fulminate; it detonates sharply when pressed with a hard body, or when heated a little above 100° C. When touched with a hot wire upon a piece of glass or thin metal, it gives a sharp report and shatters the plate, whilst mercuric fulminate emits a dull sound, and does not shatter unless closed in. A glass plate may be converted into a mirror, as stated above, by sifting mercuric fulminate upon it through a piece of muslin and firing with a match. Silver fulminate is used in toy crackers, such as the *pull crackers*, where it is mixed with powdered glass to increase the friction, and the *throw-down crackers*, where it is twisted up in thin paper with some fragments of quartz-pebble. It is occasionally mixed with mercuric fulminate in detonating tubes, to raise the note of the report.

Warm ammonia dissolves silver fulminate, and deposits, on cooling, crystals of *silver-ammonium fulminate*, $\mathrm{NH_4O.CN.O.NCAg}$, which is even more violently explosive, and is dangerous while still moist. A similar compound is formed with mercuric fulminate. Potassium chloride, added to a hot solution of silver fulminate, removes only half the silver as precipitated chloride, and the solution deposits shining plates of *silver-potassium fulminate*, KO.CN.O.NCAg, which is very explosive. By the careful addition of nitric acid, the K may be replaced by H, and the *silver-hydrogen fulminate*, HO.CN.O.NCAg, obtained, which dissolves easily in boiling water and crystallises on cooling; by boiling with silver oxide, it is converted into silver fulminate, or, with mercuric oxide, into silver-mercury fulminate.

Zinc and copper fulminates may be obtained by decomposing moist mercuric fulminate with those metals; they are soluble, crystalline, and explosive.

Sodium fulminate, $NaO.CN.ONCNa.2Aq$, is obtained by the action of sodium amalgam on an aqueous solution of mercuric fulminate. On evaporating over lime and sulphuric acid, the sodium salt is deposited in prisms which explode when rubbed. A crystalline compound of single molecules of sodium fulminate and mercuric fulminate, and 4Aq, has been obtained.

505. *Fulminuric* or *isocyanuric acid*, $HO.NC(OC.NH)_2$, is obtained as a potassium salt by boiling mercuric fulminate with potassium chloride, potassium fulminate being formed first; $2(KO)_2(CN)_2 + 3H_2O = KO.NC(OC.NH)_2 + KHO + K_2CO_3 + NH_3$ On adding silver nitrate, the sparingly soluble silver fulminurate crystallises out, and by decomposing this with H_2S, and evaporating the filtrate, a solution of the acid is obtained, which crystallises with difficulty, and is soluble in alcohol.

When *silver fulminurate*, $AgO.NC(OC.NH)_2$, is heated with strong HCl, in a sealed tube, to 110° C., it yields hydroxylamine hydrochloride, $NH_2.OH.HCl$, corresponding to one-third of the nitrogen present, and ammonium chloride corresponding to the other two-thirds. The fulminurates are feebly explosive.

It will be noticed that fulminuric acid is metameric with cyanuric acid, $(CN)_3(OH)_3$.

506. PHENOLS. —The phenols, or *oxybenzenes*, or *hydroxybenzenes*, are derived from benzene and its homologues by replacing the benzene-hydrogen atoms by hydroxyl—*e.g.*, *phenol*, $C_6H_5.OH$; *orcin*, $C_6H_3.CH_3.(OH)_2$; *pyrogallol*, $C_6H_3(OH)_3$. If the hydroxyl is introduced into the methyl group instead of the phenyl group in the homologues of benzene (p. 476), an alcohol is produced; thus, $C_6H_5.CH_2(OH)$ is *benzyl alcohol*, whereas $C_6H_4(OH).CH_3$ is *methyl phenol*, or *cresol*.

Phenols are distinguished from alcohols in combining more readily with alkalies, which caused them originally to be mistaken for acids. Thus, *sodium phenylate*, $C_6H_5.ONa$, is formed when phenol is dissolved in sodium hydrate, whereas *sodium ethylate*, $C_2H_5.ONa$, must be prepared by decomposing alcohol with sodium. Again, they do not yield aldehyds and acids when oxidised; and when acted on by nitric and sulphuric acids, they yield substitution-products, whereas the alcohols yield ethereal salts; thus, phenol yields *trinitrophenol*, or *picric acid*, $C_6H_2(NO_2)_3.OH$, and *phenol-sulphonic acid*, $C_6H_4.OH.SO_2.OH$. The phenols have a great tendency to produce coloured products of oxidation, and ferric salts generally colour them intensely.

Phenol, or *phenic acid*, or *carbolic acid*, or *hydroxybenzene*, $C_6H_5.OH$, is extracted from that portion of the heavy oil of coal-tar which boils between 150° C. and 200° C. This is allowed to cool, when it deposits crystals of naphthalene, and is then well stirred with caustic soda of sp. gr. 1.34. On standing, two layers are formed, the upper consisting of the higher homologues of benzene, and the lower of an aqueous solution of sodium phenylate. This is diluted with water, and exposed to air, when tarry oxidation-products separate, and the liquid is neutralised by successive additions of sulphuric acid, which first precipitates more tarry matters, then cresol and other homologues of phenol, and finally phenol itself as a light oil, which is purified by fractional distillation, the portion distilling between 180° C. and 190° C. being collected and artificially cooled, when the phenol crystallises out.

Phenol is present in small quantity in urine, and in the trunk, leaves, and cones of the Scotch fir. It may be produced by the action of hydric peroxide on benzene; $C_6H_5.H + HO.OH = C_6H_5.OH + HOH$. Benzene may also be directly oxidised to phenol by mixing it with aluminium chloride and passing oxygen gas (see p. 477). Benzene-sulphonic acid (p. 476), when distilled with fused potash, yields phenol—

$$C_6H_5.SO_2.OH + KOH = C_6H_5.OH + KHSO_3.$$

Properties of phenol.—Phenol crystallises in needles, often several inches long, which smell strongly of coal-tar. It fuses at 42° C. and boils at 182° C. Fused phenol is slightly heavier than water. It requires 15 parts of cold water to dissolve it, and dissolves easily in alcohol and ether. It becomes pink or brown when kept, from the presence of some impurity. When two molecules of phenol (198 parts) are heated with one molecule (18 parts) of water, and cooled to 4° C., six-sided prisms of *phenol aquate*, $(C_6H_5.OH)_2Aq$, are obtained, which fuse at 16° C. (61° F.), and dissolve easily in water. The commercial *carbolic acid crystals* generally consist of the aquate, and soon become liquid when the bottle is placed in warm water. It has a great tendency to remain superfused after cooling, solidifying suddenly on opening the bottle. The homologues of phenol, which accompany it in coal-tar, do not form crystalline aquates. Carbolic acid blisters the skin immediately; it is very poisonous, and arrests fermentation and putrefaction, so that it is largely used as an antiseptic. *MacDougall's disinfectant* is a mixture of phenol with calcium sulphite. *Calvert's disinfecting powder* consists of clay, with 12 or 15 per cent. of phenol.

When phenol vapour is passed through a red-hot tube, it yields benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene. The aqueous solution of phenol gives a purple-blue colour with ferric chloride. With ammonia and chloride of lime, it gives a blue colour. With the mixture of mercuric nitrate and nitrous acid obtained by dissolving mercury in cold nitric acid, it gives a yellow precipitate, which dissolves with a dark-red colour in nitric acid.

Sulphuric acid (concentrated), to which 6 per cent. of potassium nitrite has been added, gives a brown colour, changing to green and blue when gently heated with phenol. This is a general *reaction for identifying phenols.*

Bromine-water added to an aqueous solution of phenol produces a pale yellow precipitate of *tribromophenol*, $C_6H_2Br_3.OH$, which redissolves until the bromine is in excess. This affords an excellent qualitative and quantitative test for phenol. If the precipitate be warmed with water and sodium amalgam, sodium phenylate is produced, which gives the smell of phenol when heated with dilute sulphuric acid.

507. By passing phenol vapour over heated zinc-dust, it is converted into benzene; $C_6H_5.OH + Zn = C_6H_6 + ZnO$. This is a *general method for the conversion of phenols into the corresponding hydrocarbons.*

Phenol forms a crystalline compound with CO_2, which is only stable under pressure, and may be obtained by heating salicylic acid in a sealed tube to 260° C.; $C_6H_4(OH).CO_2H = C_6H_5.OH.CO_2$.

Potassium-phenol, $C_6H_5.OK$, is a soluble crystalline body obtained by heating phenol with potassium or its hydrate or carbonate.

Sodium-phenol is obtained in a similar way, and is used for the manufacture of salicylic acid (see p. 524). Other metals may replace the hydroxyl hydrogen of phenol.

Diphenyl oxide, or *phenyl ether*, $C_6H_5.O.C_6H_5$, is obtained by distilling phenol with aluminium chloride. Aluminium phenol is first formed; $6O_6H_5OH + Al_2Cl_6 = (C_6H_5O)_6Al_2 + 6HCl$; this is afterwards decomposed into alumina and diphenyl oxide, $(C_6H_5O)_6Al_2 = Al_2O_3 + 3(C_6H_5)_2O$. It forms prisms, fusing at 28° C. and boiling at about 250° C. It smells like the geranium leaf, and is remarkable for its stability under the influence of oxidising and reducing agents. Water does not dissolve it, but alcohol and ether do so.

Double ethers may be obtained which contain alcohol radicals and phenyl. *Phenyl-methyl ether*, $C_6H_5.O.CH_3$, is prepared by passing methyl chloride through sodium phenol at 200° C. It is a fragrant liquid, of sp. gr. 0.991, boiling at 152°. This ether is identical with *anisol*, obtained by distilling anisic acid (p. 525) with baryta. Anisic acid is thus shown to be a phenyl and methyl derivative, as implied by its systematic name of methyl-(para)oxybenzoic acid, its formula, $C_6H_4.CH_3.O.CO_2H$, showing it to be derived from benzoic (or *phenyl carboxylic*) acid, $C_6H_5.CO_2H$, through salicylic or hydroxybenzoic, $C_6H_4.HO.CO_2H$, by the replacement of the hydroxyl hydrogen in the latter by methyl. When anisic acid is distilled with baryta, $C_6H_4.CH_3.O.CO_2H + BaO = BaCO_3 + C_6H_5.O.CH_3$. Salicylic acid yields phenol when distilled with baryta; $C_6H_4.HO.CO_2H + BaO = C_6H_5.OH + BaCO_3$. Benzoic acid yields benzene—

$$C_6H_5.CO_2H \ + \ BaO \ = \ C_6H_5.H \ + \ BaCO_3.$$

Methyl salicylate, or wintergreen oil, $C_6H_4.HO.CO_2.CH_3$, is metameric with anisic acid, and also yields phenyl-methyl ether when distilled with baryta. Hydriodic acid heated to 140° C. with anisol, in a sealed tube, converts it into phenol and methyl iodide; $C_6H_5O.CH_3 + HI = C_6H_5.OH + CH_3I$.

When ethyl salicylate is distilled with baryta, it yields *phenyl-ethyl ether*, $C_6H_5.O.C_2H_5$.

508. Phenol is not acted on by acids, as alcohol is, yielding ethereal salts, but corresponding phenyl compounds are obtained by indirect processes. When phenol is heated with phosphoric chloride, it yields *fluorobenzene* and *phenyl orthophosphate;* the formation of chlorobenzene proves the existence of hydroxyl in phenol; $C_6H_5.OH + PCl_5 = PCl_3O + C_6H_5.Cl + HCl$. The phenyl orthophosphate results from the action of more phenol upon the phosphoryl chloride—

$$PCl_3O \ + \ 3C_6H_5OH \ = \ PO(C_6H_5O)_3 \ + \ 3HCl.$$

The orthophosphate, which may also be written $(C_6H_5)_3PO_4$, crystallises in needles, fusing at 45° C., soluble in alcohol and ether, and, without change, in strong sulphuric acid. *Phenyl-phosphoric acid*, $H_2C_6H_5PO_4$, and *diphenyl-phosphoric acid*, $H(C_6H_5)_2PO_4$, are formed when phosphoric anhydride acts on phenol. The formation of *phenyl-phosphoric chloride*, $PO(OC_6H_5)Cl_2$, and *diphenyl-phosphoric chloride*, $PO(OC_6H_5)_2Cl$, by the action of phosphoryl chloride on phenol, renders it probable that the above acids are, respectively, $PO(OC_6H_5)(OH)_2$ and $PO(OC_6H_5)OH$.

Phenyl carbonate, $CO(OC_6H_5)_2$, results from the action of $COCl_2$ on phenol at 150° C.; $2HOC_6H_5 + COCl_2 = CO(OC_6H_5)_2 + 2HCl$. Alcohol deposits it in needles fusible at 78° C. Some *phenyl chlorocarbonate*, $CO.Cl.OC_6H_5$, is formed at the same time, and if this be dissolved in ether and treated with ammonia, *phenyl carbamate*, $CO.NH_2.OC_6H_5$, may be obtained in crystals from the ethereal solution: $CO.Cl.OC_6H_5 + 2NH_3 = CO.NH_2.OC_6H_5 + NH_3.HCl$. When heated with NH_3 to 140° C., it yields phenol and urea; $CO.NH_2.OC_6H_5 + NH_3 = CO(NH_2)_2 + HO.C_6H_5$.

Phenyl-sulphuric acid is unknown; *potassium phenylsulphate*, $SO_2.OC_6H_5.OK$, is obtained by the prolonged action of potassium disulphate on phenol dissolved in potash; $C_6H_5.OK + 2SO_2OHOK = SO_2.OC_6H_5.OK + SO_2(OK)_2 + H_2O$. The product is extracted with hot alcohol, from which it crystallises in tables soluble in water. It is decomposed by exposure to moist air, or by boiling with water or dilute HCl, yielding phenol and hydropotassium sulphate—

$$SO_2.OC_6H_5.OK \ + \ HOH \ = \ HO.C_6H_5 \ + \ SO_2.OH.OK.$$

Potassium phenylsulphate is found in the urine in small quantity.

Phenyl acetate, $C_6H_5.C_2H_3O_2$, may be obtained by the action of acetyl chloride on phenol (again proving the presence of the HO group); $C_6H_5.OH + C_2H_3O.Cl = C_6H_5.OC_2H_3O + HCl$. It is a liquid of peculiar smell, and boils at 193° C. A piece of hard glass tube becomes invisible in phenyl acetate, its index of refraction for light being the same as that of the liquid.

Phenyl oxalate, $(C_6H_5)_2C_2O_4$, is obtained by heating phenol with dried oxalic acid and phosphoryl chloride; $2C_6H_5OH + H_2C_2O_4 + POCl_3 = (C_6H_5)_2C_2O_4 + HPO_3 + 3HCl$. It is insoluble in water, but crystallises in prisms from alcohol.

Phenyl hydrosulphide, or *thiophenol*, or *phenyl-mercaptan*, $C_6H_5.SH$, is formed by the action of phosphoric sulphide on phenol—

$$8C_6H_5OH \ + \ P_2S_5 \ = \ 2C_6H_5SH \ + \ 2(C_6H_5)_3PO_4 \ + \ 3H_2S.$$

It has an offensive odour, and boils at 170° C. Its extra-radical hydrogen is replaceable by metals, as usual with mercaptans. With mercuric oxide, it yields *mercuric thio-phenol*, $(C_6H_5S)_2Hg$. When mixed with ammonia and exposed to air, phenyl hydrosulphide is converted into *diphenyl disulphide*, a crystalline solid; $2C_6H_5SH + O = (C_6H_5)_2S_2 + H_2O$. *Diphenyl sulphide*, $(C_6H_5)_2S$, is obtained by distilling sodium benzene-sulphonate with P_2S_5. It is an offensive liquid, boiling at about 280° C. Nitric acid converts it into *sulphobenzide*, $(C_6H_5)_2SO_2$, which is also produced by the action of sulphuric anhydride on benzene—

$$2C_6H_5H \ + \ 2SO_3 \ = \ (C_6H_5)_2SO_2 \ + \ H_2SO_4.$$

509. *Phenyl-chloride*, or *chlorobenzene*, C_6H_5Cl, *phenyl bromide*, or *bromobenzene*, C_6H_5Br, and *phenyl iodide*, or *iodobenzene*, C_6H_5I, are obtained by the action of the halogens on benzene, and are liquids boiling at 132° C., 154° C., and 185° C. respectively.

Fluorobenzene, C_6H_5F, has been obtained by the action of hydrofluoric acid on benzene di-azopiperidide, and is a liquid of sp. gr. 1.024, boiling at 84° C.

510. Phenyl, like the alcohol radicals, forms organo-mineral compounds. *Mercury di-phenyl*, $Hg(C_6H_5)_2$, is formed when sodium amalgam acts on bromobenzene. It is a fusible crystalline solid, subliming almost unchanged, insoluble in water, and sparingly soluble in alcohol and ether, but soluble in benzene. When heated, in a sealed tube, with $HgCl_2$ and alcohol, it yields *mercury-phenyl chloride*, HgC_6H_5Cl, and by decomposing this with silver hydrate, *mercury-phenyl hydroxide*, $HgC_6H_5.OH$, is obtained as a crystalline strongly alkaline base.

511. When mercury diphenyl is heated with phosphorous chloride to 180° C., it yields *phos-phenyl dichloride*, $PC_6H_5Cl_2$, a liquid which combines with chlorine to form crystals of *phos-phenyl tetrachloride*, $PC_6H_5Cl_4$. When phos-phenyl dichloride is decomposed by water, it gives *phos-phenylous acid*, a crystalline monobasic acid which forms a white insoluble ferric salt. This acid might be expected to contain two hydroxyl groups replacing the Cl_2 in phos-phenyl dichloride, but when it is heated with phosphoric chloride, it yields *phos-phenyl oxychloride*, $C_6H_5POCl_2$, showing that the formula of the acid is $C_6H_5.PHO(OH)$, and the action of phosphoric chloride upon it is $C_6H_5.PHO(OH) + 2PCl_5 = C_6H_5PClO.Cl + POCl_3 + PCl_3 + 2HCl$.

Phos-phenyl tetrachloride, when decomposed by water, gives *phos-phenylic acid*, $C_6H_5PO(OH)_2$, a crystalline dibasic acid, which is decomposed at 100° C. into benzene and metaphosphoric acid, HPO_3. When acted on by nitric acid, it yields *nitro-phos-phenylic acid*, $C_6H_4.NO_2.PO(OH)_2$, and this gives *amido-phos-phenylic acid*, $C_6H_4.NH_2.PO(OH)_2$, when reduced by tin and hydrochloric acid. Acted on by N_2O_3, in a nitric solution, this yields *di-azophosphenylic acid nitrate*, $C_6H_4.N_2.NO_3.PO(OH)_2$, a colourless crystalline explosive body, giving yellow solutions in water and alcohol, and forming yellow and red explosive salts. When phosphenyl dichloride is treated with hydriodic acid, and the solid product $(PC_6H_5I_2.HI)$ decomposed by alcohol, it yields *phenyl-phosphine*, or *phosphaniline*, $PH_2.C_6H_5$, a liquid of intense and repellent odour, boiling at 160° C., and absorbing oxygen from the air to form the soluble crystalline *phenyl-phosphine oxide*, $C_6H_5.PH_2O$. Phenyl-phosphine combines with HI to form *phenyl-phosphonium iodide*, $PH_3C_6H_5I$, which yields a crystalline platinum-salt. *Di-ethyl-phenyl-phosphine*, $PC_6H_5(C_2H_5)_2$, is a liquid boiling at 220° C., resulting from the action of zinc ethide on phosphenyl dichloride. It combines with ethyl iodide to form *tri-ethyl-phenyl-phosphonium iodide*, $PC_6H_5(C_2H_5)_3I$, the solution of which, when boiled with silver oxide, yields the corresponding hydrate, $PC_6H_5(C_2H_5)_3OH$, as a crystalline base.

When phosphenyl dichloride is exposed to moist air, it deposits a yellow insoluble body, $P_4HC_6H_5$, corresponding to solid hydric phosphide, P_4H_2. *Diphenyl-phosphine*, $PH(C_6H_5)_2$, is produced by acting with sodium hydrate on *diphenyl phosphorous chloride*, $PCl(C_6H_5)_2$, which is a result of the action of mercury phenyl on phosphenyl dichloride. Diphenyl phosphine is a liquid, boiling at 280° C. It has an offensive odour, and does not exhibit basic properties. *Methyl-diphenyl-phosphine*, $PCH_3(C_6H_5)_2$, is a liquid, boiling at 284° C., formed when zinc methyl acts on $PCl(C_6H_5)_2$.

Triphenyl-phosphine, $P(C_6H_5)_3$, is formed by the action of sodium on chlorobenzene and phosphorous chloride dissolved in ether; $3C_6H_5Cl + PCl_3 + Na_6 = P(C_6H_5)_3 + 6NaCl$. It forms yellow crystals, having little smell, fusing at 79° C., and boiling, in an atmosphere of nitrogen, at about 360° C., with slight decomposition. It dissolves in alcohol and ether, and in strong HCl, from which water precipitates it. Chlorine does not act upon it, even when heated. By dissolving it in hot hydriodic acid, *triphenyl-phosphonium iodide*, $P(C_6H_5)_3HI$, may be crystallised; it is decomposed by water. By treating triphenyl-phosphine with HCl and $KClO_3$, it is converted into $P(C_6H_5)_3(OH)_2$, which loses H_2O at 100° C., becoming *triphenyl-phosphine oxide*, $P(C_6H_5)_3O$, a solid, fusing at 154° C., and boiling at 360° C. The corresponding sulphide, $P(C_6H_5)_3S$, crystallises from a solution of the phosphine and sulphur in CS_2. The nitrate, $P(C_6H_5)_3(NO_3)_2$, crystallises from solution of triphenyl-phosphine in strong nitric acid.

Triphenyl-phosphine combines readily with the iodides of alcohol radicals; thus, with methyl iodide, it forms *triphenyl-methyl-phosphonium iodide*, $P(C_6H_5)_3CH_3I$; when this is decomposed by silver hydrate, the corresponding hydroxide is produced at first, but this soon decomposes into benzene and methyl-diphenyl-phosphine oxide; $P(C_6H_5)_3CH_3.OH = C_6H_5.H + P(C_6H_5)_2CH_3.O$, showing that the third phenyl group is less strongly attached to the phosphorus than the methyl group.

Methylene-hexphenyl-phosphonium iodide, $P_2(C_6H_5)_6(CH_2)''I_2$, formed on the type $2NH_4I$, is obtained from triphenyl-phosphine and methylene iodide, CH_2I_2. The corresponding ethylene compound is also known.

By acting on triphenyl-phosphine oxide with a mixture of nitric and sulphuric acid, the tri-nitro-compound $P(C_6H_4.NO_2)_3O$ is obtained, which is reduced by tin and HCl to the amido-compound $P(C_6H_4.NH_2)_3O$, which crystallises in red plates from hot water, and forms soluble salts. By boiling this with acetic anhydride, half of the amido-hydrogen may be exchanged for acetyl, producing the compound $P(C_6H_4.NH.C_2H_3O)_3O$, which fuses at 186° C. without decomposing.

Diphosphenyl, or *phosphobenzene*, $C_6H_5P_2C_6H_5$, is prepared by acting on phenyl-phosphine with phosphenyl dichloride in an atmosphere of hydrogen—

$$PH_2C_6H_5 + PC_6H_5Cl_2 = C_6H_5P_2C_6H_5 + 2HCl.$$

It is a yellow crystalline body, soluble in benzene. It corresponds in composition to azobenzene, but is less stable, becoming converted into $(C_6H_5P)_2O$.

512. The *arsen-phenyl compounds* correspond, for the most part, to the phosphorus compounds, but the *arsen-phenyl dichloride*, $AsC_6H_5Cl_2$, is not decomposed by water, even on boiling.

Boro-phenyl dichloride, $BC_6H_5Cl_2$, is prepared like the corresponding phosphorus compound. When decomposed by water, it yields crystallised *boro-phenylous* or *phenylboric acid*, $BC_6H_5(OH)_2$, which has powerful antiseptic properties, as would be expected from its connexion with boric acid and phenol, both strongly antiseptic compounds. Boro-phenylous acid, even when dissolved in 25,000 parts of water, gives a precipitate of *phenyl mercuric chloride* on adding solution of mercuric chloride; $HgCl_2 + BC_6H_5(OH)_2 + H_2O = HgC_6H_5Cl + HCl + B(OH)_3$.

The *silicon-phenyl compounds* have a special interest on account of the resemblance of silicon to carbon. *Silico-phenyl trichloride*, $Si^{iv}C_6H_5Cl_3$, prepared by heating mercury diphenyl with silicon tetrachloride, is a fuming liquid boiling at 197° C. When decomposed by water, it yields *silico-benzoic acid*, $C_6H_5.Si.O.OH$, or benzoic acid, $C_6H_5.CO_2H$, in which carbon is replaced by silicon—

$$SiC_6H_5Cl_3 + 2H_2O = SiC_6H_5.O.OH + 3HCl.$$

The acid is soluble in ether, like benzoic, and is left on evaporation as a transparent glass which fuses at 92° C. When distilled with potash, it yields benzene and potassium silicate, just as benzoic acid yields the carbonate—

$$C_6H_5.SiO_2H + 2KOH = C_6H_5.H + K_2SiO_3 + H_2O.$$

The silicobenzoates have not been prepared. *Tri-ethyl-silicon-phenyl*, $SiC_6H_5(C_2H_5)_3$, formed by heating the trichloride with zinc-ethyl, is a liquid boiling at 230° C. *Silicon tetraphenyl*, $Si(C_6H_5)_4$, the analogue of methane, is obtained by the action of sodium on chlorobenzene and silicon tetrachloride dissolved in ether, with a little acetic ether to start the action. It is sparingly soluble in alcohol and ether, but may be crystallised from benzene. It fuses at 228° C., and boils above 360° C. When ignited, it burns entirely away, the SiO_2 being carried off in light flakes.

513. Tin also forms organo-metallic phenyl-compounds, obtained by similar methods; *tri-ethyl-tin-phenyl*, $Sn^{iv}C_6H_5(C_2H_5)_3$, a liquid, boiling at 254° C., is prepared by the action of sodium on ethereal solution of bromobenzene and tin-triethyl iodide, $Sn(C_2H_5)_3I$. Strong HCl converts it into $C_6H_5.H$ and $Sn(C_2H_5)_3Cl$.

Tin-diphenyl-dichloride, $Sn(C_6H_5)_2Cl_2$ is obtained by boiling stannic chloride and mercury-diphenyl with petroleum spirit; it crystallises in prisms which yield stannic chloride and benzene with strong HCl. The corresponding oxide,

$Sn(C_6H_5)_2O$, and hydroxychloride, $Sn(C_6H_5)_2.OH.Cl$ have been obtained. *Tin-triphenyl chloride*, $Sn(C_6H_5)_3Cl$, has also been prepared.

Antimony-triphenyl, $Sb(C_6H_5)_3$, is a crystalline body obtained by the action of sodium on bromobenzene and antimonious chloride dissolved in benzene.

514. *Diphenyle* or *phenyl-phenyle*, $C_6H_5.C_6H_5$, is prepared by the action of sodium on bromobenzene dissolved in ether; $2C_6H_5Br + Na_2 = (C_6H_5)_2 + 2NaBr$. It may also be obtained by passing benzene vapour over red-hot pumice-stone; $2C_6H_5H = (C_6H_5)_2 + H_2$; or by distilling potassium phenol with potassium benzoate—

$$C_6H_5.OK + C_6H_5.CO_2K = (C_6H_5)_2 + K_2CO_3;$$

potassium oxalate may be substituted for benzoate; $2C_6H_5OK + (COOK)_2 = (C_6H_5)_2 + 2CO(OK)_2$. It is also found among the last products of the distillation of coal-tar (at about 260° C.). Diphenyl crystallises from alcohol or ether in leafy crystals which have a pleasant odour and are insoluble in water. It fuses at 70° C., and boils at 254° C. When it is dissolved in glacial acetic acid, and treated with chromic acid, one of the C_6H_5 groups is destroyed, while the other forms benzoic acid, $C_6H_5.CO_2H$. One atom of hydrogen in diphenyl may be replaced by other radicals, producing *chloro-diphenyl*, $C_{12}H_9Cl$, *bromo-diphenyl*, $C_{12}H_9Br$, *cyano-diphenyl*, $C_{12}H_9CN$, *nitro-diphenyl*, $C_{12}H_9NO_2$, and *amido-diphenyl*, $C_{12}H_9NH_2$.

Imido-diphenyl, or *carbazol*, $C_6H_4(NH)''C_6H_4$, is formed when phenylamine (aniline) vapour is passed through a red-hot tube; $2NH_2C_6H_5 = (C_6H_4)_2NH + NH_3 + H_2$. It is also obtained at the end of the distillation of coal-tar, and as a secondary product in the preparation of aniline. It crystallises in plates, fusing at 238° C., and boiling at 354° C.; it is soluble in alcohol and ether. *Acridine*, isomeric with carbazol, accompanies it in coal-tar, but fuses at 107° C., and combines with acids. It has a very irritating action on the skin.

Diphenyl-sulphonic acid, $C_{12}H_9.SO_2.OH$, and *diphenyl-disulphonic acid*—

$$C_{12}H_8(SO.OH)_2,$$

are obtained when diphenyl is heated with sulphuric acid; the former is characterised by the insolubility of its copper salt. When these are distilled with potash, they yield *phenyl-phenol*, $C_{12}H_9.OH$, or $C_6H_4.C_6H_5.OH$, and *diphenol*, $C_{12}H_8(OH)_2$, or $HO(C_6H_4)_2OH$. *Diphenylene oxide*, $(C_6H_4)_2O$, is formed when phenol is heated with lead oxide; $2C_6H_5OH + PbO = (C_6H_4)_2O + 2H_2O + Pb$. It is insoluble in water, but crystallises from alcohol and ether; it has a pleasant smell, fuses at 80° C., and boils at 287° C.

Cœrulignone, $C_{12}H_4(OCH_3)_4(O_2)''$, is obtained among the products of distillation of wood; it is insoluble in ordinary solvents, but crystallises from phenol in blue needles. It was formerly called *cedriret*, from *cedria*, pitch, and *rete*, a net, in allusion to its interlaced crystals. Tin and hydrochloric acid convert it into *hydro-cœrulignone*, $C_{12}H_4(OCH_3)_4(OH)_2$, which forms colourless crystals. When this is heated to 200° C. with HCl, it yields methyl chloride and hexhydroxy-diphenyl; $C_{12}H_4(OCH_3)_4(OH)_2 + 4HCl = 4CH_3Cl + C_{12}H_4(OH)_6$; this compound forms silvery crystals which dissolve in potash with a blue colour; when heated with zinc-dust, it is reduced to diphenyl, $(C_6H_5)_2$.

515. *Methene-diphenyl*, or *diphenyl-methane*, $CH_2(C_6H_5)_2$, or *benzyl-benzene*, $C_6H_5(C_7H_7)$, is obtained by heating a mixture of benzene and benzyl chloride with zinc-dust; $2C_6H_5H + 2(C_6H_5.CH_2.Cl) + Zn = 2C_6H_5(C_7H_7) + ZnCl_2 + H_2$. It crystallises in needles which smell like the orange, and dissolve in alcohol and ether; it fuses at 26° C., and boils at 261° C. Potassium dichromate and sulphuric acid oxidise it to *diphenyl-ketone*; $C_6H_5.CH_2.C_6H_5 + O_2 = C_6H_5.CO.C_6H_5 + H_2O$. By substituting phenol for benzene in the preparation of diphenyl-methane, *benzyl-phenol*, $C_6H_5.C_7H_6(OH)$, is obtained in crystals, fusing at 84° C. This is isomeric with *benzhydrol*, $C_6H_5.CH(OH).C_6H_5$ produced by the action of sodium amalgam on an alcoholic solution of *benzophenone* (diphenyl-ketone).

Diphenyl-ketone accompanies the benzene obtained by distilling calcium benzoate; $(C_6H_5.CO_2)_2Ca = C_6H_5.CO.C_6H_5 + CaCO_3$. It may also be obtained by heating benzoic acid with benzene and P_2O_5; $C_6H_5.CO.OH + C_6H_5.H + P_2O_5 = C_6H_5.CO.C_6H_5 + 2HPO_3$. It crystallises in prisms which are insoluble in water, but dissolve in alcohol.

Diphenic acid $(C_6H_4)_2(CO_2H)_2$ is obtained by oxidising phenanthrene, $C_{14}H_{10}$ (p. 480), with CrO_3. When distilled with lime, it yields *diphenylene-ketone*, $(C_6H_4)CO(C_6H_4)$, which, when heated with zinc-dust, gives *diphenylene-methane*, or *fluorene*, $(C_6H_4)CH_2(C_6H_4)$, which is found in the last runnings (300°–305°) from coal-tar, and crystallises from alcohol with a blue fluorescence. When oxidised it is reconverted into the ketone. Nascent hydrogen converts it into the secondary alcohol, *diphenylene-carbinol*, or *fluorene alcohol*, $(C_6H_4)_2.CH.OH$.

516. *Chlorophenol*, $C_6H_4Cl.OH$, and the corresponding bromine and iodine substitution-products are obtained by the action of those elements on phenol. *Nitrophenol*, $C_6H_4(NO_2)OH$, *dinitrophenol*, $C_6H_3(NO_2)_2.OH$, and *trinitrophenol*, $C_6H_2(NO_2)_3.OH$, are produced when nitric acid acts on phenol. The last is known as *picric acid* (p. 540). *Nitrosophenol*, $C_6H_4(NO)OH$, is produced by a very indirect process. By reducing nitrophenols with tin and HCl, the NO_2 group is converted into the NH_2 group, and *amido-phenols* are produced. Dinitro- and trinitrophenols admit of a partial conversion of the NO_2 groups, so that *amido-nitro-phenols* are found.

Picramic-acid, or *amido-dinitrophenol*, $C_6H_2(NO_2)_2NH_2.OH$, is prepared by reducing ammonium picrate in alcoholic solution by passing hydric sulphide, evaporating to dryness, and decomposing the ammonium picramate with acetic acid—

$$C_6H_2(NO_2)_3.ONH_4 + 3H_2S = C_6H_2(NO_2)_2NH_2.ONH_4 + 2H_2O + S_3.$$

The picramic acid crystallises in red needles, which fuse at 165° C. It is soluble in water and alcohol, forming red solutions, which become blood-red on adding an alkali. The change of the yellow colour of potassium picrate to the dark red of potassium picramate by the action of a reducing agent in the presence of excess of potash, is employed in the examination of urine for the detection and estimation of glucose, which easily converts the picrate into picramate when heated. The picramates of potassium and ammonium form dark red crystals. Silver picramate is a red precipitate.

517. *Phenol-sulphonic*, $C_6H_4.OH.SO_2OH$, and *phenol-disulphonic acid*—

$$C_6H_3.OH(SO_2OH)_2,$$

are obtained by dissolving phenol in strong sulphuric acid, $SO_2.OH.OH$, of which one of the OH groups removes an atom of phenol-hydrogen, forming HOH, and replacing it by the *sulphuric acid residue*, $SO_2.OH$.

Phenyl-phenylene sulphonic acid, $C_6H_5.C_6H_4.SO_2OH$, is formed when sulphuric acid acts on diphenyl, $(C_6H_5)_2$. When fused with potash, it yields *phenyl-phenol*, $C_6H_4.C_6H_5.OH$, a crystalline solid, which vaporises easily with steam—

$$C_6H_5.C_6H_4.SO_2OH + KOH = SO.OH.OK + C_6H_4.C_6H_5.OH.$$

When benzene-sulphonic acid, $C_6H_5.SO_2OH$ (p. 476), is treated with nitric acid, it is converted into *nitrobenzene-sulphonic acid*, $C_6H_4.NO_2.SO_2OH$, which may also be produced with nitrobenzene, $C_6H_5.NO_2$, and fuming sulphuric acid. By the action of reducing agents, this becomes *amidobenzene-sulphonic acid*, or *sulphanilic acid*, $C_6H_4.NH_2.SO_2OH$, which is a product of the action of sulphuric acid on aniline, $C_6H_5.NH_2$. Nitrous acid converts amidobenzene-sulphonic acid into *di-azobenzene-sulphonic acid*; $C_6H_4.NH_2.SO_2OH + HNO_2 = C_6H_4.N.N.SO_3 + 2H_2O$ (see p. 582). When the potassium-salt of this acid is treated with sulphurous acid, it yields the potassium salt of *phenyl-hydrazine-sulphonic acid*—

$$C_6H_4.N.N.SO_3K + 2H_2SO_3 + 2H_2O = C_6H_5.NH.NH_2.SO_3K + 2H_2SO_4.$$

518. *Phenyl-hydrazine*, $C_6H_5.NH.NH_2$, or *phenyl-imide-amide*, is prepared by dissolving aniline (1 part by weight) in strong hydrochloric acid (20 parts), cooling by adding ice, and slowly adding an ice-cold solution of sodium nitrite (0.75 parts) in water (4 parts). The aniline hydrochloride is thus converted into di-azobenzene chloride—

$$C_6H_5NH_2.HCl + HNO_2 = C_6H_5N.N.Cl + 2H_2O.$$

A solution of stannous chloride (4.5 parts) in an equal weight of hydrochloric acid is now carefully added; this converts the di-azobenzene chloride into phenyl-hydrazine hydrochloride, which is precipitated—

$$C_6H_5N.N.Cl + 4HCl + 2SnCl_2 = C_6H_5.NH.NH_2.HCl + 2SnCl_4.$$

The precipitate is washed with a mixture of alcohol and ether, dissolved in a little water, and decomposed by strong NaHO, when the hydrazine falls as an oily layer, which is freed from water by distilling with potassium carbonate.

Phenyl-hydrazine is thus obtained as a colourless aromatic liquid of sp. gr. 1.091, and boiling point 234° C. It solidifies in a freezing mixture, forming tabular crystals fusing at 23° C. It is sparingly soluble in cold water, but dissolves in alcohol and ether. Phenyl-hydrazine is a strong reducing agent and absorbs oxygen from air, becoming brown. It reduces alkaline cupric solution, *even in the cold*, precipitating yellow cuprous hydrate, and evolving nitrogen, while aniline and benzene are found in the solution. This is a *general reaction for identifying hydrazines*, and may also be employed for di-azo compounds by boiling their aqueous solutions with hydropotassium sulphite, to reduce them to hydrazines, and adding potash and alkaline cupric solution. It also reduces mercuric oxide in the cold, forming nitrogen, aniline, benzene, and mercury-diphenyle. Solution of phenyl-hydrazine hydrochloride mixed with sodic acetate forms a *general test for aldehyds and ketones*, with which it forms insoluble oily or crystalline compounds, thus precipitating them from their aqueous solutions. It is a monacid base, and forms crystalline salts.

Phenyl-hydrazine represents a class of organic compounds which contain a tetratomic group composed of two atoms of triatomic nitrogen, $=N—N=$. They may be regarded as derived from a di-amidogen group, $H_2N.NH_2$. When one atom of H in this group is replaced by a radical, as in the case of phenyl-hydrazin, a *primary hydrazine* is formed, while the displacement of H_2 gives a *secondary hydrazine*, such as *diphenyl hydrazine*, $(C_6H_5)_2N.NH_2$, which is metameric with *hydrazobenzene*—

$$C_6H_5.HN_2H.C_6H_5.$$

When phenyl hydrazine acts upon ethyl aceto-acetate, it yields water and an oil having the composition $C_{12}H_{16}N_2O_2$—

$$C_6H_8N_2 + CH_2.C_2H_3O.CO_2.C_2H_5 = H_2O + C_{12}H_{16}N_2O_2.$$

This substance is decomposed at 100° C. into alcohol and *oxymethylquinizine*, $C_{10}H_{10}N_2O$, a fusible, volatile, crystalline solid. When this is heated, in a sealed tube, with methyl iodide and methyl hydrate, it is converted into *dimethyloxyquinizine*, $C_{11}H_{12}N_2O$, or *antipyrine*, which crystallises in needles, fusing at 113° C., and giving a green crystalline precipitate with nitrous acid. This substance is used in medicine as a febrifuge.

Hydrazine, $(NH_2)_2$, has been recently obtained as a strongly alkaline gas, very soluble in water, and having a peculiar odour, only slightly resembling that of ammonia. It is a powerful reducing agent, and forms salts with the acids.

519. DIPHENOLS, OR DIHYDROXYBENZENES.—*Pyrocatechin*, $C_6H_4(OH)_2$, may be obtained by fusing phenol-sulphuric acid with potash—

$$C_6H_5.SO_2OH + KOH = C_6H_4(OH)_2 + KHSO_2.$$

It is found among the products of distillation of *catechu*, an astringent body extracted by boiling water from the inner bark wood of *Acacia catechu*, and used in tanning. *Kino*, a similar extract from certain varieties of Pterocarpus, an Indian tree of the same botanical order, also furnishes it; as do most vegetable extracts which contain tannin. The leaves of the Virginia creeper, a plant of the vine order, contain pyrocatechin. It is present in crude pyroligneous acid distilled from wood, and is said to be formed when cellulose, starch, or sugar is heated between 200° and 280° C. Pyrocatechin crystallises in prisms which fuse at 102° C., and boil at 245° C., though it begins to sublime below its fusing point. It is very soluble in water, alcohol, and ether. It is a reducing agent, precipitating Cu_2O from alkaline cupric solutions on warming, and reducing silver nitrate in the cold. In presence of alkalies it absorbs oxygen from the air, becoming brown. With ferric chloride, it gives a green colour, changed to red by alkalies. Nitric acid oxidises it to oxalic acid. It has weak acid properties, and was formerly called *oxyphenic acid*.

Guaiacol, or *methylpyrocatechin*, $C_6H_4.OH.OCH_3$, may be obtained by distilling *guaiacum*, a resinous exudation from the West Indian tree, called *lignum vitæ*.

The distillate is dissolved in ether, and mixed with alcoholic potash, which produces a crystalline mass of *potassium guaiacol*, which is washed with ether and decomposed by dilute sulphuric acid. It is also produced by heating to 180° C. a mixture of pyrocatechin, potassium sulphomethylate, and potash—

$$C_6H_4(OH)_2 + KCH_3SO_4 + KOH = C_6H_4.OH.OCH_3 + K_2SO_4 + HOH.$$

Beech-wood kreasote also contains it. Guaiacol is a colourless aromatic liquid of sp. gr. 1.12, boiling at 200° C. It mixes sparingly with water, but easily with alcohol. It gives an emerald-green colour with ferric chloride, and acts as a reducing agent in alkaline solutions. When heated with hydriodic acid, it yields methyl iodide and pyrocatechin; $C_6H_4.OH.OCH_3 + HI = C_6H_4(OH)_2 + CH_3I$. It has the properties of a weak acid. When potassium guaiacol is heated with methyl iodide, it yields *veratrol*, or *methyl guaiacol*; $C_6H_4.OK.OCH_3 + CH_3I = C_6H_4(OCH_3)_2 + KI$. Veratrol is an aromatic liquid, which may also be obtained by heating with baryta the *veratric* (*dimethyl-protocatechuic*) acid, extracted from sabadilla seeds (p. 602); $C_6H_3(OCH_3)_2.CO_2H + BaO = C_6H_4(OCH_3)_2 + BaCO_3$.

520. *Resorcin*, $C_6H_4(OH)_2$, is another dihydroxybenzene (*meta*) or phenol, which was named from *resin*, being obtained from several bodies of that class, and *orcin*, with which it is homologous. It is now prepared on a large scale for the manufacture of colours by the action of caustic alkalies on benzene-disulphonic acid. This acid is prepared by gradually adding benzene (4 parts) to fuming sulphuric acid, sp. gr. 2.244 (15 parts), gently heating for some hours, and finally to 275° C.; $C_6H_6 + 2H_2SO_4 = C_6H_4(SO_2.OH)_2 + 2H_2O$. The *benzene* (*meta*) *disulphonic acid* forms a deliquescent crystalline mass on cooling. This is dissolved in a large quantity of water, neutralised with lime, and strained from the calcium sulphate formed by the excess of sulphuric acid. The solution of calcium benzene-disulphonate is decomposed by Na_2CO_3, the precipitated $CaCO_3$ filtered off, the solution evaporated to dryness, and the residue of sodium benzene-disulphonate fused with 2½ times its weight of caustic soda, at 270° C., for eight or nine hours; $C_6H_4(SO_2.ONa)_2 + 2NaOH = C_6H_4(OH)_2 + 2SO_3Na_2$. The fused mass is dissolved in hot water, and boiled with HCl till all the SO_2 is expelled. The resorcin is then extracted from the cooled aqueous solution by agitation with ether, and is obtained in crystals when the ether is distilled off.

Resorcin is obtained in considerable quantity by distilling *extract of Brazil wood*, a dye made by boiling the wood of *Cæsalpinia braziliensis* with water, and evaporating the solution. It was originally prepared by fusing with potash the gum-resin known as *galbanum*, obtained in Turkey and the East Indies as an exudation from the *Galbanum officinale*, an umbelliferous plant. Other gum-resins obtained from plants of the same order also yield resorcin when fused with potash; such as *ammoniacum*, *assafœtida*, *sagapenum*, all more or less fœtid-smelling medicinal bodies imported from the East. When these gum-resins are distilled alone, they yield *umbelliferone*, $C_9H_6O_3$, or $C_6H_4(CHO)_2CO$, which is converted into resorcin when fused with potash.

Resorcin, or *resorcinol*, crystallises in prisms or tables which fuse at 118° C., and boil at 276° C., but may be sublimed at a much lower temperature. It has a sweet taste, and is easily soluble in water, alcohol, and ether. Its solution gives a violet colour with ferric chloride. Exposed to air, it absorbs oxygen and becomes brown. Ammoniacal copper and silver solutions are reduced when heated with it. The most characteristic test for resorcin consists in heating it with phthalic anhydride (p. 536), dissolving in dilute sulphuric acid, and adding ammonia, when a splendid green fluorescence is produced, due to the formation of *resorcin-phthalein*, or *fluorescein*, $C_6H_4(CO.C_6H_3(OH)_2)_2$.

The resorcin of commerce sometimes contains *thioresorcin* $C_6H_4(SH)_2$, which may be obtained by reducing *benzene disulphonic chloride*, $C_6H_4(SO_2Cl)_2$, with tin and hydrochloric acid.

Styphnic acid, or *trinitroresorcin*, $C_6H(NO_2)_3(OH)_2$, so named from its astringent taste (στύφνος), is prepared by dissolving resorcin in strong sulphuric acid, and gradually adding strong nitric acid; after standing for some hours, water is added, which precipitates the acid. Styphnic acid is also produced by the action of nitric acid on extract of Brazil-wood and on those gum-resins which yield resorcin on fusion with potash, as well as on *Purrée*, or *Indian yellow*, a compound of magnesia with *euxanthine*, $C_{19}H_{16}O_{10}$. It was formerly called *oxypicric acid*, since it contains one atom of oxygen more than picric acid or trinitro phenol, $C_6H_2(NO_2)_3.OH$, which it much resembles. Styphnic acid forms yellow six-sided prisms or tables, sparingly soluble in cold water, but dissolving in alcohol and ether. It fuses at 175° C., and explodes when strongly heated, though it sublimes when heated gradually. It is a dibasic acid, and forms salts which are more explosive than the picrates. Ferrous sulphate and lime-water give a green colour with styphnic acid, and a blood-red with picric acid.

521. *Pyrogallin*, or *pyrogallol*, or *trihydroxybenzene*, $C_6H_3(OH)_3$, formerly called *pyrogallic acid*, is a phenol obtained by heating gallic acid; $C_6H_2(OH)_3.CO_2H = C_6H_3(OH)_3 + CO_2$. To prepare it, gallic acid, dried at 100° C., is mixed with three times its weight of powdered pumice-stone, to equalise the heat, and distilled in a retort through which a slow stream of CO_2 is passed, the retort being heated by an oil-bath to between 210° and 220° C. A much better yield is obtained by heating the gallic acid with 2½ parts of water in a digester (*autoclave*) to the above temperature for half an hour. The solution thus obtained is decolorised by animal charcoal and crystallised.

A solution of pyrogallol, for use as a developer in photography, may be prepared by heating 10 grammes of gallic acid with 30 c.c. of glycerine to 195° C. as long as CO_2 is evolved, and making up to a litre with water.

Pyrogallin may be sublimed from nut-galls heated to about 215° C., when the tannin is decomposed into pyrogallin and carbon dioxide: $C_{13}H_9O_7.CO_2H + H_2O = 2C_6H_3(OH)_3 + 2CO_2$. It may be obtained synthetically by fusing *chlorophenol-sulphonic acid* with potash—

$$C_6H_3Cl.OH.SO_3H + 2KOH = C_6H_3(OH)_3 + KCl + KHSO_3.$$

Pyrogallin crystallises in fine needles, which are felted together in light white tufts. It fuses at 115° C. and boils at 210° C. It is very soluble in water (2½ parts), alcohol, and ether. When its solution is mixed with an alkali, it at once absorbs oxygen from the air, becoming brown, and forming carbonate, acetate, and other products, a little carbonic oxide being evolved. A mixture of potash and pyrogallin is employed to absorb oxygen in gas analysis. Pyrogallin is a strong reducing agent, precipitating silver and mercury in the metallic state; its action on silver-salts renders it useful in photography and in hair-dyeing. A pure ferrous salt gives no colour with pyrogallin, but a trace of ferric salt causes a blue coloration, while a pure ferric salt gives a red colour. When heated with phthalic anhydride, it yields *pyrogallol phthalein*, or *gallein*; $C_6H_4(CO.C_6H_2(OH)_3)_2$, which is used as a red dye. When chlorine is passed through a cooled solution of pyrogallin in acetic acid, *trichloro-pyrogallin*, $C_6Cl_3(OH)_3$, is obtained, and may be crystallised in needles.

Phloroglucol, $C_6H_3(OH)_3$, isomeric with pyrogallol, was first obtained from a glucoside called phloridzin, existing in the bark of the apple-tree; the *glucol* refers to its sweet taste. It is also made, like resorcinol, by fusing certain vegetable extracts and gum-resins with caustic potash. It is thus obtained from *gamboge*, the resinous juice of *Cambogia gutta* (Ceylon), from *dragon's blood*, the resin of *Dracæna draco*, from *kino* (p. 635), *catechu*, and from the yellow dye-wood, *fustic*. The residue of the preparation of extract of fustic is fused with potash and a little water, dissolved in water, acidified with sulphuric acid, and shaken with ether, which extracts phloroglucol and protocatechuic acid; the ether is distilled off, and the aqueous solution of the residue mixed with lead acetate to precipitate the protocatechuic acid. The lead is precipitated by H_2S, and the phloroglucol again extracted by ether. It may also be prepared by fusing resorcin (1 part) with soda (6 parts) until the mass has a light chocolate colour, when it is treated as above, omitting the separation of protocatechuic acid.

Phloroglucol is formed by fusing *benzene-trisulphonic acid*, $C_6H_3(SO_2.OH)_3$, with soda.

Phloroglucol crystallises in prisms with 2Aq, which it loses at 100° C. It fuses at 220°, and may be sublimed; it dissolves easily in water, alcohol, and ether, and reduces alkaline cupric solution. Ferric chloride gives a violet colour. Its solution in hydrochloric acid stains wood violet-red, and is an excellent test for woody tissue. Alkaline solutions of phloroglucol are oxidised by air, and become brown. When dissolved in ammonia, it yields a crystalline base; $C_6H_3(OH)_3 + NH_3 = H_2O + C_6H_3.NH_2(OH)_2$ (*phloramine*). Other phenols do not so readily exchange OH for NH_2.

When phloroglucol is dissolved in acetic acid and treated with potassium nitrite, at a low temperature, it yields, on addition of excess of potash and alcohol, green needles of a very explosive body, which is the *potassium salt of tri-nitroso-phloroglucol*, $C_6O_3(NOK)_3$. When this is gradually added to a mixture of nitric and sulphuric acids, it is converted into *trinitro-phloroglucol*, $C_6(NO_2)_3(OH)_3$, which crystallises in yellow explosive prisms, and dyes wool and silk yellow like picric acid. It is a tribasic acid, and forms three series of coloured salts.

Hex-hydroxy-benzene, $C_6(OH)_6$, has been obtained by a circuitous process. It is crystalline, sparingly soluble in cold water, alcohol, and ether; the solutions absorb oxygen, becoming violet, and reduce silver nitrate. It is converted into benzene by distillation with zinc-dust.

522. *Cresol*, or *methyl-phenol*, or *hydroxytoluene*, $C_6H_4.CH_3.OH$, accompanies phenol in coal-tar. The *coal-tar kreasote* is a mixture of phenol and cresol. Cresol may be prepared by dissolving toluidine in sulphuric acid, adding potassium nitrite, and distilling by steam—

$$C_6H_4.CH_3.NH_2 + HNO_2 = C_6H_4.CH_3.OH + 2H_2O + N_2.$$

There are three isomeric cresols prepared from the corresponding toluidines.

Orthocresol is solid, fuses at 31° C., and boils at 185° C. *Metacresol* is liquid, and boils at 195° C. *Paracresol* is solid, fusing at 36° C., and boiling at 198° C. They are metameric with benzyl-alcohol, $C_6H_5.CH_2.OH$. Paracresol occurs in urine, and is a product of the putrefaction of albumen. Meta- and paracresol give a blue colour with ferric chloride.

Wood-tar creasote contains phenol, cresol, *phlorol*, $C_6H_3(CH_3)_2.OH$, guaiacol, and *creosol*, $C_6H_3(OCH_3)CH_3.OH$. This last is obtained from that portion of the tar which distils over at 220° C., by dissolving it in ether, and adding very strong potash, which precipitates potassium-creosol, from which creosol is separated by sulphuric acid. It is an aromatic liquid, which yields *acetyl-creosol*, $C_6H_3(OCH_3)CH_3(OC_2H_3O)$, when treated with acetyl chloride, and this, when oxidised by potassium permanganate, becomes *acetyl-vanillic acid*, $C_6H_3(OCH_3)(OC_2H_3O)CO_2H$, from which vanillic acid may be obtained by treatment with caustic soda.

523. *Orcin*, or *orcinol*, or *dihydroxytoluene*, $C_6H_3.CH_3(OH)_2$, is preprepared from certain lichens, which are used by dyers for preparing the colours known as *litmus*, *cudbear*, and *archil*; such as *Lecanora tar-*

tarea, or *rock-moss*, *Roccella tinctoria*, or *orchella-weed*, and others. The lichens are boiled with lime and water for some time, the solution filtered, evaporated to one-fourth, treated with CO_2 to precipitate the lime, and shaken with ether to extract the orcin. Some orcin appears to exist ready formed in the lichens, but the greater part of it is formed by the action of the lime and water upon certain acids, which may be extracted from the lichens by lime in the cold, and obtained as gelatinous precipitates by hydrochloric acid. Thus, *orsellinic acid*, $C_6H_2.CH_3(OH)_2.CO_2H$, when boiled with lime, yields carbon dioxide and orcin, $C_6H_3.CH_3(OH)_2$.

Erythric acid, $C_{20}H_{22}O_{10}$, yields orcin and erythrite (p. 499); *evernic acid*, $C_{17}H_{16}O_7$, yields orcin and *everninic acid*, $C_9H_{10}O_4$.

Evernic acid is extracted from the lichen *Evernia prunastri*.

Lecanoric acid, $C_{16}H_{14}O_7.H_2O$, when boiled with water, yields two molecules of orsellinic acid, $C_8H_8O_4$.

Orcin is also produced by the action of fused potash on aloes, the juice of a plant of the Liliaceous order (dragon's blood, obtained from the same order, yields phloroglucol). Orcin may be prepared from toluene, $C_6H_5.CH_3$, by converting it into (ortho)chlorotoluene-sulphonic acid, and fusing this with excess of potash—

$$C_6H_3Cl.CH_3.SO_3H + 2KOH = KCl + KHSO_3 + C_6H_3.CH_3(OH)_2$$

Orcin crystallises in colourless six-sided prisms, containing a molecule of water. It fuses at 58° C., becomes anhydrous at 86°, and boils at 290° C. It tastes sweet and dissolves in water, alcohol, and ether; ferric chloride colours it violet. It forms a crystalline compound with a molecule of ammonia, and when its solution in ammonia is exposed to air, it absorbs oxygen, giving a purple solution, from which acetic acid precipitates a red colouring matter, *orcéin*;

$$C_7H_8O_2 \text{ (orcin)} + NH_3 + O_3 = 2H_2O + C_7H_7NO_3 \text{ (orcéin)}.$$

This substance is the chief colouring matter of the dyes prepared from lichens, by mixing them with lime and urine (to furnish ammonia), and exposing them to the air for some weeks. The colour is pressed out, and made into cakes with chalk or plaster of Paris.

Orcéin is sparingly soluble in water, but dissolves easily in alcohol and in alkaline liquids, yielding purple solutions which are reddened by acids, orcéin being precipitated.

524. QUINONES are formed from the hydrocarbons of the aromatic series by the substitution of the group –O–O– or $(O_2)''$ for H_2, and are therefore products of oxidation of the hydrocarbons.

Quinone, $C_6H_4(O_2)''$, or *benzoquinone*, may be obtained by heating benzene with chromyl chloride, when HCl is evolved and a brown solid compound produced, which is decomposed by water with formation of quinone, which remains dissolved in the excess of benzene—

$$(1)\ C_6H_6 + 2CrO_2Cl_2 = 2HCl + C_6H_4(CrO_2Cl)_2;$$
$$(2)\ C_6H_4(CrO_2Cl)_2 + H_2O = C_6H_4(O_2)'' + Cr_2O_3 + 2HCl.$$

Many benzene derivatives also yield quinone when oxidised. It is best prepared by oxidising aniline with potassium dichromate and sulphuric acid. One part of aniline is dissolved in a mixture of 8 parts of sulphuric acid with 30 parts of water, and 3½ parts of powdered potassium dichromate are slowly added to the cooled solution, which is then heated for some hours to about 35° C. After cooling, the liquid is shaken with ether, which extracts the quinone, and leaves it in golden yellow crystals when evaporated.

It is also obtained when quinic acid is oxidised with manganese dioxide and sulphuric acid; $C_6H_7(OH)_4CO_2H + O_2 = C_6H_4(O_2)'' + CO_2 + 4H_2O$. Many plant-extracts yield quinone when thus treated.

Quinone crystallises very easily in yellow prisms or plates, which sublime even in the cold, and fuse at 116° C., emitting a characteristic odour, and subliming in long golden needles in the presence of steam. It is sparingly soluble in cold water, but dissolves in hot water, and crystallises on cooling; alcohol and ether dissolve it. Its solution stains the skin brown. Quinone acts as an oxidising agent, liberating iodine from hydriodic acid, and becoming converted into *hydroquinone*, or *quinol*, $C_6H_4(OH)_2$. This is related to quinone in the same way as hydrocærulignone is related to cærulignone (p. 633), which is also a quinone. On mixing a saturated solution of hydrocærulignone with solution of quinone, an orange colour is produced, and shining blue needles of cærulignone are deposited, the quinone being reduced to hydroquinone—

$$C_{12}H_4(OCH_3)_4(OH)_2 + C_6H_4(O_2)'' = C_{12}H_4(OCH_3)_4(O_2)'' + C_6H_4(OH)_2.$$

Extremely dilute solutions of quinone will give this reaction.

Hydroquinone is a constant product of the action of reducing agents on quinone, and is best prepared by passing SO_2 through a warm saturated solution of quinone, when it is deposited in six-sided prisms, which fuse at 169° C. and sublime in monoclinic tables, so that hydroquinone is dimorphous. It is moderately soluble in water, and easily in alcohol and ether. Hydroquinone is isomeric with pyrocatechin (p. 635), but is distinguished from it by the action of oxidising agents, such as ferric chloride, which convert hydroquinone into fine green metallic prisms of *green hydroquinone*, or *quinhydrone*, $C_6H_4O_2.C_6H_4(OH)_2$, which may also be obtained by mixing aqueous solutions of quinone and hydroquinone. This beautiful substance is sparingly soluble in cold water, but dissolves in hot water to a brownish-red solution, which deposits the splendid green crystals on cooling. It dissolves in alcohol and ether with a yellow colour. When heated, it fuses to a brown liquid, and partly sublimes in green plates, the remainder decomposing and giving the yellow crystalline sublimate of quinone. On boiling its aqueous solution, quinone volatilises, and hydroquinone remains in solution. It dissolves in ammonia with a deep green colour, which becomes brown on exposure to air. Oxidising agents, such as ferric chloride, added in excess, convert quinhydrone into quinone, whilst reducing agents, such as sulphurous acid, convert it into hydroquinone. Hydroquinone occurs among the products of distillation of the succinates, and it has been produced from ethyl succinate by the following steps: Ethyl succinate, $C_2H_4(CO_2C_2H_5)_2$, acted on by sodium, yields *ethyl succinyl succinate*, $C_2H_4.C_2H_2(CO)_2.(CO_2.C_2H_5)_2$; when this is treated with bromine, hydrogen is abstracted, leaving *ethyl-quinol dicarboxylate*, $C_6H_4O_2(CO_2.C_2H_5)_2$. The acid obtained from this ethereal salt, *quinol-dicarboxylic acid*, $C_6H_4O_2(CO_2H)_2$, crystallises in needles, and yields a blue colour with ferric chloride. When distilled, it yields hydroquinone, $C_6H_4(OH)_2$, and $2CO_2$. As ethyl succinyl succinate may also be obtained by the action of sodium on ethyl bromaceto-acetate, hydroquinone may be built up from acetic acid.

Tetrachloroquinone, or *chloranil*, $C_6Cl_4(O_2)''$, is a frequent product of the action of chlorine or of a mixture of potassium chlorate and HCl upon benzene-derivatives and compounds connected with the aromatic group, such as phenol, aniline, salicin, and isatin. It may be prepared from quinone by the action of $KClO_3$ and HCl, but more cheaply from phenol, by mixing it with potassium chlorate (4 parts) and adding it gradually to hydrochloric acid diluted with an equal volume of water. The mixture is gently heated, and more chlorate added, when a yellow mixture of *trichloroquinone*, $C_6HCl_3(O_2)''$, and tetrachloroquinone is precipitated. This is treated with sulphurous acid, which reduces the quinones to hydroquinones. The *tetrachlorohydroquinone*, $C_6Cl_4(OH)_2$, is insoluble in water, whilst the *trichlorohydroquinone*, $C_6HCl_3(OH)_2$, dissolves. The former is then oxidised by strong nitric acid, which converts it into chloranil. This body, which is used in colour making, is yellow, insoluble in water, and sparingly soluble in alcohol; ether and benzene dissolve it, and deposit it in yellow crystals which may be sublimed. It is unattacked even by concentrated acids. Potash dissolves it with a purple colour, and yields purple crystals of potassium chloranilate; $C_6Cl_4O_2 + 4KOH = 2KCl + 2H_2O + C_6Cl_2(OK)_2O_2$. By dissolving the sparingly soluble potassium salt in hot water, and adding HCl, a red crystalline body is precipitated, which is *chloranilic acid*, $C_6Cl_2(OH)_2O_2.Aq$. It is soluble in water, with a violet colour, but sulphuric or hydrochloric acid precipitates it from the aqueous solution.

Bromanil, $C_6Br_4(O_2)''$, has also been obtained from phenol.

525. *Naphthoquinone*, $C_{10}H_6(O_2)''$, is prepared by dissolving naphthalene (1 part) $C_{10}H_8$, in glacial acetic acid (6 parts) and oxidising with chromic anhydride (3 parts) dissolved in glacial acetic acid (2 parts). The mixture is boiled, and distilled after adding more water, when the naphthoquinone passes over with the steam. It is insoluble in water, sparingly soluble in cold alcohol, but dissolves in hot alcohol and in ether, crystallising in yellow tables, which fuse at 125° C. and sublime below 100°. It has the quinone smell. Alkalies dissolve it, and it is oxidised by strong nitric acid into phthalic acid, $C_6H_4(CO_2H)_2$. When heated with hydriodic acid and amorphous phosphorus, naphthoquinone is converted into *naphtho-hydroquinone*, $C_{10}H_6(OH)_2$.

Anthraquinone, $C_{14}H_8O_2$, is prepared by dissolving anthracene, $C_{14}H_{10}$, in glacial acetic acid, and adding chromic anhydride to the hot solution; on adding water, the anthraquinone is precipitated, and may be purified by sublimation. It sublimes in yellow needles which are sparingly soluble in alcohol and ether, but dissolve in hot benzene and in nitric acid. It fuses at 273° C. Potash does not dissolve it, but when fused with potash, it yields potassium benzoate. Sulphurous acid does not convert it into a hydroquinone, nor does hydriodic acid, but the latter reduces it to anthracene. Hence it is not a true quinone, as was formerly believed. It is, in fact, a double ketone, $C_6H_4(CO)_2C_6H_4$, which accounts for its conversion into potassium benzoate by fusion with potash—

$$(C_6H_4)_2(CO)_2 + 2KOH = 2(C_6H_5.CO.OK).$$

Moreover, when distilled with soda-lime it yields benzene—

$$(C_6H_4)_2(CO)_2 + 4NaOH = 2C_6H_6 + 2CO(ONa)_2.$$

It may be obtained synthetically by heating phthalyl dichloride with benzene and zinc-dust; $C_6H_4(COCl)_2 + C_6H_6 + Zn = (C_6H_4)_2(CO)_2 + ZnCl_2 + H_2$. When anthraquinone is heated with zinc-dust alone, it yields anthracene. Bromine converts it into *dibromanthraquinone*, $C_6H_4(CO)_2C_6H_2Br_2$, and when this is heated to about 180° C. with potash, it yields *potassium alizarate*, $C_6H_4(CO)_2C_6H_2(OK)_2$; from the aqueous solution of this, hydrochloric acid precipitates *alizarin*—

$$C_6H_4(CO)_2C_6H_2(OH)_2,$$

a red body, which is prepared from *madder*, the root of *Rubia tinctorum*.

Alizarin, one of the chief vegetable dyes, was formerly obtained exclusively from this plant, imported from the South of France and the Levant. It does not occur ready formed in the plant, but is produced by the decomposition of *ruberythric acid*, $C_{26}H_{28}O_{14}$, which may be extracted from madder root by cold water, and crystallises in yellow prisms. When the root is allowed to ferment, or is treated with sulphuric acid, the ruberythric acid undergoes hydrolysis, and is converted into alizarin and glucose—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

Alizarin may be prepared from anthraquinone by converting it into the sulphonic acid and fusing this with potash.

The anthraquinone is made on the large scale by treating anthracene, in leaden tanks, with potassium dichromate and diluted sulphuric acid, the reaction being completed by boiling. The anthraquinone is dissolved in strong sulphuric acid, and reprecipitated by water, which retains the impurities in solution. After being washed and dried, it is heated for eight or ten hours to 180° C. with fuming sulphuric acid in an iron pot, being constantly stirred; on diluting with water, any unaltered anthraquinone is precipitated, and anthraquinone sulphonic acid remains in solution; $(C_6H_4)_2(CO)_2 + SO_2(OH)_2 = C_6H_4(CO)_2.C_6H_3.SO_2.OH + HOH$. By neutralising the solution with caustic soda, the sparingly soluble sodium anthraquinone sulphonate is obtained, and this is converted into sodium alizarate by heating with caustic soda and some potassium chlorate to furnish oxygen—

$$C_6H_4(CO)_2.C_6H_3.SO_2.ONa + 2NaOH + O = C_6H_1(CO)_2.C_6H_2(ONa)_2 + NaHSO_3 + HOH.$$

In order to prepare alizarin from anthracene without previous conversion into anthraquinone, the anthracene is exposed in leaden chambers to the action of chlorine, which converts it into a bright yellow crystalline mass of dichloranthracene, $C_{14}H_8Cl_2$. This is heated to 260° C. with strong sulphuric acid, in an iron pot, until a sample dissolves in water without fluorescence. A mixture of anthraquinone-sulphonic and disulphonic acids is thus produced by the following reactions;

$$C_{11}H_8Cl_2 + 2HSO_4 = C_{11}H_6(SO_3H)_2Cl_2 \text{ (\textit{dichloranthracene-disulphonic acid})} + 2H_2O;$$
$$C_{14}H_6(SO_3H)_2Cl_2 + H_2SO_4 = C_{11}H_6(SO_3H)_2(O_2)'' \text{ (\textit{anthraquinone-disulphonic acid})} + 2HCl + SO_2;$$
$$C_{11}H_8Cl_2 + H_2SO_4 = C_{14}H_8O_2 + 2HCl + SO_2; \quad C_{11}H_8O_2 + H_2SO_4 = C_{11}H_7(SO_3H)O_2 + H_2O.$$

The mixed sulphonic acids are neutralised with lime, and the calcium salts are decomposed by sodium carbonate. The concentrated solution of the sodium salts is heated with caustic soda and a little potassium chlorate, in a closed iron boiler, to about 180° C. for twenty-four hours, when a purple solution is obtained, containing the alizarate and anthrapurpurate of sodium; $C_{14}H_7(SO_3H)O_2 + 4NaOH = Na_2SO_3 + 2H_2O + H + C_{14}H_6(NaO)_2O_2$ (*sodium alizarate*); $C_{11}H_6(SO_3H)_2O_2 + 7NaOH = C_{14}H_5(NaO)_3O_2$ (*sodium anthrapurpurate*) $+ 2Na_2SO_3 + 4H_2O + H_2$.

The solution is run into dilute sulphuric acid, when a mixture of alizarin and anthrapurpurin is obtained as a yellow precipitate. The potassium chlorate is added in order to oxidise some *sodium oxanthraquinonate*, $C_{11}H_7(NaO)O_2$, resulting from a secondary reaction; it is converted into sodium alizarate by sodium hydrate and oxygen; $C_{14}H_7(NaO)O_2 + NaHO + O = C_{11}H_6(NaO)_3O_2 + H_2O$.

Properties of alizarin.—It is very sparingly soluble in water, but easily soluble in alcohol and ether, and crystallises in orange-coloured prisms which contain 3Aq, and become red when dried. It fuses at about 275° C., and may be sublimed. It dissolves in strong sulphuric acid with a deep red colour, and is precipitated by water. It acts like a dibasic acid, dissolving in alkalies to purple solutions, which give purple-blue precipitates with salts of barium and calcium. The insolubility and brilliant colours of the alizarates are of great value in dyeing and calico-printing. Alizarin gives red precipitates (*madder lakes*) with salts of tin and aluminium, and a dark violet with salts of iron.

When heated with zinc-dust, alizarin is converted into anthracene, an observation which led to its artificial formation from that body. Nitric acid oxidises it to phthalic acid—

$$C_6H_4(CO)_2C_6H_2(OH)_2 + O_{13} = C_6H_4(CO.OH)_2 + 6CO_2 + H_2O.$$

Anthrapurpurin, $C_6H_3.OH.(CO)_2.C_6H_2(OH)_2$, is formed as above mentioned in the preparation of alizarin, and may be obtained by oxidising alizarin with MnO_2 and H_2SO_4. It resembles alizarin, but fuses at a higher temperature (330° C.), and is more soluble in water. The colours of its metallic salts are more brilliant than those given by alizarin, so that its presence in the artificial dye is advantageous.

Purpurin, or *tri-hydroxy-anthraquinone*, $C_6H_4(CO)_2.C_6H(OH)_3$, is metameric with the preceding, and is found accompanying alizarin in old madder root, and may be separated from it by boiling with alum, which dissolves only the purpurin. It may also be obtained by oxidising natural alizarin with MnO_2 and H_2SO_4.

Flavo-purpurin, $C_6H_3.OH(CO)_2.C_6H_2(OH)_2$, is sometimes formed in the manufacture of alizarin. It crystallises in golden needles soluble in alcohol.

Anthrachrysone, or *tetra-hydroxy-anthraquinone*—

$$C_6H_2(OH)_2(CO)_2C_6H_2(OH)_2,$$

is obtained by heating dihydroxybenzoic acid, $C_6H_3(OH)_2.CO.OH$, with sulphuric acid, which abstracts the elements of $2H_2O$ from two molecules of the acid.

Rufigallic acid, or *hex-oxy-anthraquinone*, $C_6H(OH)_3(CO)_2C_6H(OH)_3$ (see p. 527), is prepared by heating gallic acid with sulphuric acid, which removes the elements of $2H_2O$ from two molecules of gallic acid, $C_6H_2(OH)_3.CO.OH$. It is used as a red dye.

All these anthracene derivatives yield that hydrocarbon when heated with zinc-dust.

526. The hydrocarbons which furnish quinones when oxidised form an homologous series, increasing by C_4H_2.

Benzene	C_6H_6	Benzoquinone	$C_6H_4(O_2)''$
Naphthalene	$C_{10}H_8$	Naphthaquinone	$C_{10}H_6(O_2)''$
Anthracene	$C_{14}H_{10}$	Anthraquinone	$C_{14}H_8(O_2)''$
Chrysene	$C_{18}H_{12}$	Chrysoquinone	$C_{18}H_{10}(O_2)''$
Idrialene	$C_{22}H_{14}$	Idriquinone	$C_{22}H_{12}(O_2)''$

These hydrocarbons are products of the distillation of coal, and the quinones give rise to important artificial colouring matters.

527. CARBOHYDRATES.—The compounds belonging to this class contain hydrogen and oxygen in the proportion to form water, combined with six atoms, or some multiple of six atoms, of carbon. They are remarkable for the number of instances of isomerism which they present, and may be divided into three groups, the members of each group having the same empirical formula, viz.—

Sucroses, or *saccharoses*, $C_{12}H_{22}O_{11}$ | *Glucoses*, $C_6H_{12}O_6$ | *Amyloses*, $C_6H_{10}O_5$.

Most of the carbohydrates are *optically active*—that is, they rotate the plane of polarisation of a ray of polarised light either to right or left, those which effect a rotation to the right being termed *dextrorotatory*, and to the left, *lævorotatory*.

The sucroses are converted into glucoses by boiling with dilute sulphuric or hydrochloric acid; $(C_6H_{11}O_5)_2O$ (*sucrose*) + $H_2O = 2C_6H_{12}O_6$ (*glucose*). Cane-sugar, so treated, yields a mixture of equal parts of grape-sugar, or *dextrose*, and fruit-sugar, or *lævulose*, and, since the lævorotatory power of the latter predominates in the mixture, the dextrorotatory cane-sugar is said to have been *inverted*.

Milk-sugar, $C_{12}H_{22}O_{11}$, is not inverted by boiling with acids, but gives dextrose and galactose, both having the composition $C_6H_{12}O_6$, and both rotating the plane of polarisation to the right.

The amyloses are converted into glucoses when boiled with sulphuric or hydrochloric acid; $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$.

528. *Cane-sugar*, or *sucrose*, $C_{12}H_{22}O_{11}$, is not found only in the sugar-cane, but in many other plants, such as beet-root, maize, barley, almonds, walnuts, hazel-nuts, coffee-beans, and madder root. It occurs also in the sap of the maple, lime, birch, and sycamore, as well as in the juices of many fruits; in these, it is generally accompanied by *invert-sugar*. During the early period of vegetation, it appears that grape-sugar and fruit-sugar are formed, and that these become cane-sugar during the

ripening. The green sugar-cane contains much dextrose and lævulose, which are afterwards converted into sucrose. *Honey* contains cane-sugar and invert-sugar, in varying proportions, depending on the food of the bees.

To extract sugar from plants, they should be cut up, dried at a temperature not exceeding 100° C., and boiled repeatedly with alcohol of sp. gr. 0.87, which will deposit the sugar in crystals, on cooling.

On the large scale, sugar is manufactured by crushing the cane between rollers, when an acid juice is obtained, containing about 20 per cent. of sucrose; this is neutralised by lime, to prevent inversion of the sugar, and heated to coagulate the albumen. This is skimmed off the surface, and the syrup is evaporated till it is strong enough to crystallise. About half the sugar is thus obtained in brown crystals (*moist sugar*), the remainder being partly extracted as an inferior sugar (*foots sugar*) by another evaporation, and partly left as uncrystallisable sugar in the *molasses* or *treacle*. To *refine* the raw sugar, it is dissolved in water, decolorised by filtering through a thick bed of animal charcoal, and evaporated at 60° C. (140° F.) in a copper *vacuum-pan* connected with an air-pump, since a higher temperature would invert the sugar. It may then be obtained in large crystals, *sugar-candy*, or, by stirring, in minute crystals which are drained in conical moulds, and washed with a saturated solution of sugar till they form white *loaf-sugar*.

Sugar is extracted by a similar process from the juice of the white beet-root. The juice contains about 10 per cent. of sugar, about half of which is obtained in a crystallised state.

A larger yield of crystallisable sugar has been obtained from cane and beet juice by the *strontia process*, which consists in precipitating the sugar from the boiling solution by adding strontium hydrate; the precipitate, $C_{12}H_{22}O_{11}(SrO)_2$, is washed with hot water, and afterwards suspended in boiling water and allowed to cool, when most of the strontia is deposited as hydrate, and the remainder is precipitated from the solution by CO_2.

Sometimes the potassium salts which are present in the molasses, and hinder crystallisation, are precipitated in the form of alum by adding aluminium sulphate.

Properties of sucrose.—It crystallises in monoclinic prisms, which are insoluble in absolute alcohol, but dissolve to almost any extent in boiling water. 100 parts of saturated syrup at 20° C. contain 67 of sugar. Sucrose fuses at 160° C. (320° F.), and does not crystallise on cooling. If kept melted for some time, it becomes converted into a mixture of grape-sugar (dextrose) and *lævulosan*; $C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5$. If this be dissolved in water, and yeast added, the dextrose ferments, but the lævulosan is unaltered. When further heated, but below 190° C. (374° F.), sucrose loses $2H_2O$ and becomes brown, yielding *caramelan*, $C_{12}H_{18}O_9$, an amorphous, brittle, very deliquescent body, colourless when pure, and not capable of reconversion into sugar. Commercial *caramel*, used for colouring liquids, is a mixture of this with other bodies formed at higher temperatures, and is usually made by heating starch-sugar. It is bitter.

Subjected to destructive distillation, sucrose yields acetic acid, aldehyd, acetone, $CH_4.CO.CO_2$, &c., leaving a shining porous charcoal. When distilled with lime, it gives acetone, metacetone, phorone, acetylene, &c. *Metacetone*, $C_6H_{10}O$, is isomeric with mesityle oxide, obtained by the action of H_2SO_4 upon acetone, C_3H_6O, but that liquid boils at 132° C., while metacetone boils at 84° C. *Phorone*, $C_9H_{14}O$, is also obtained by the action of dehydrating agents on acetone; it forms yellow prisms smelling like geraniums.

When sugar is melted in a little water (barley-water was formerly used), it cools to a glassy mass (barley-sugar) enclosing a little water; this dissolves some of the sugar, and deposits it in crystals, until in course of time the whole mass is opaque and crystalline. Heated with water to 160° C., sucrose yields formic acid, carbon dioxide, and charcoal. At 280° C. some pyrocatechin is produced. Dilute acids, even carbonic, convert sucrose into dextrose and lævulose, slowly in the cold, and quickly on heating.

Fused with potash, sucrose gives the potassium-salts of oxalic, formic, acetic, and propionic acids, together with acetone and metacetone.

Sucrose acts as a reducing agent; if ammonio-nitrate of silver be added to its solution, followed by sodium hydrate, a mirror of silver will be deposited on heating. The antiseptic properties of sucrose are well known; a strong syrup arrests fermentation. Weak solution of sucrose, in contact with yeast, is first converted into dextrose and lævulose, and then into alcohol and carbon dioxide (see p. 487). Sugar absorbs ammonia gas, forming $C_{12}H_{21}(NH_4)O_{11}$, which decomposes again on exposure to air.

Sucrose behaves like a weak acid to strong bases. *Sodium sucrate*, $C_{12}H_{21}NaO_{11}$, is precipitated when strong caustic soda is added to an alcoholic solution of sugar. Slaked lime is easily dissolved by solution of sugar; if equal molecules of sugar and lime be dissolved in cold water, and alcohol added, a precipitate of $CaO.C_{12}H_{22}O_{11}$ is obtained, but if an excess of lime be employed, the precipitate is $2CaO.C_{12}H_{22}O_{11}$. When the solution of either of these is boiled, it deposits $3CaO.C_{12}H_{22}O_{11}$, which requires more than 100 parts of cold water and 200 parts of boiling water to dissolve it, but dissolves readily in solution of sugar. All these compounds are decomposed by CO_2.

If strontium hydrate be added to a boiling solution containing 15 per cent. of sucrose, the compound $2SrO.C_{12}H_{22}O_{11}$, separates as a granular precipitate, and when 2.5 molecular weights of the hydrate have been added, the precipitation of the sugar is nearly complete. If the precipitate be stirred with boiling water, it will decompose, on cooling, forming sugar and strontium hydrate (see p. 644).

Iron is much corroded by sugar, in the presence of air, the metal being dissolved as *ferrous sucrate*, $C_{12}H_{20}Fe''O_{11}$ (?), which, in contact with air and moisture, deposits ferric hydrate, and is reconverted into sugar, which attacks a fresh portion of the iron. Lead is also attacked and dissolved by sugar solution, especially when heated. On boiling lead hydrate with solution of sugar, it is dissolved, and, as the solution cools, it deposits *diplumbic sucrate*, $C_{12}H_{18}Pb_2O_{11}.Aq$, as a white powder, which loses its water at 100° C. The sugar may be completely precipitated in this form. *Triplumbic sucrate*, $C_{12}H_{16}Pb_3O_{11}$, is precipitated when soda is added to a mixture of solutions of lead acetate and sugar; it may be crystallised in needles from sugar solution.

Many metallic oxides form compounds with sugar which are readily soluble in alkalies, so that the addition of sugar to solutions of copper and iron, for example, will prevent their precipitation by potash, soda, or ammonia. If solution of sucrose be mixed with cupric sulphate, and potash gradually added, a blue precipitate of cupric hydrate is formed, which dissolves, when more potash is added, to a deep blue liquid, which may be heated to boiling without change, but if long boiled or kept, it deposits cuprous oxide or hydrate as a red or yellow precipitate.

When a solution containing sugar with one-fourth of its weight of common salt is allowed to evaporate spontaneously, it deposits deliquescent rhombic prisms of $C_{12}H_{22}O_{11}.NaCl.2Aq$.

Strong sulphuric acid converts dry sucrose into a brown mass, but if water be present, or if heat be applied, the mixture froths up and blackens, evolving CO, CO_2, and SO_2 gases. Dilute sulphuric and hydrochloric acids, when boiled with sugar, convert it into a brown substance, partly soluble in alkalies, and containing about 63 per cent. of carbon (sugar contains 42). Formic acid (containing only 26 per cent. of carbon) is found in the solution. Strong nitric acid dissolves sucrose, and converts it, on heating, into oxalic and saccharic acids. When heated with dilute nitric acid, it yields, beside these, acetic, tartaric, hydrocyanic, and carbonic acids, with evolution of N, NO, and N_2O_3. A cold mixture of strong nitric and sulphuric acids converts sugar into a resinous mass, which is insoluble in water and soluble in alcohol. It explodes when heated or struck, and appears to be *sucro-tetra-nitrin*, $C_{12}H_{18}O_7(NO_3)_4$.

When heated with an excess of acetic anhydride, sucrose exchanges eight atoms of hydrogen for eight atoms of acetyle; thus, $C_{12}H_{22}O_{11} + 8(C_2H_3O)_2O = C_{12}H_{14}(C_2H_3O)_8O_{11} + 8(C_2H_3O.OH)$. The new compound might be regarded as an ethereal acetate, representing sucrose as an *octahydric alcohol*, $C_{12}H_{14}O_3(OH)_8$, but its easy conversion by dilute acids and by yeast into dextrose and lævulose, both having the formula $C_6H_{12}O_6$, induces the belief that it resembles the ethers in constitution, and should be represented by $((C_6H_7(OH)_4O_2)$, which breaks up into two pentahydric alcohols by hydrolysis; $((C_6H_7(OH)_4O)_2O + H_2O = 2C_6H_7O(OH)_5$.

Its decomposition by heat into dextrose and lævulosan would then be explained by the equation $(C_6H_7(OH)_4O)_2O = C_6H_7O(OH)_5$ (*dextrose*) + $C_6H_7O_2(OH)_3$ (*lævulosan*).

529. *Milk-sugar, or lactose*, $C_{12}H_{22}O_{11}$, is prepared by evaporating the whey of milk to a syrup, and setting it aside in a cold place to crystallise. The commercial product is generally crystallised round strings or slender wooden rods. It is purified by dissolving it in water and precipitating by alcohol. The crystals contain a molecule of water of crystallisation, which they lose at 130° C. Lactose is much less sweet and less soluble than sucrose, requiring 6 parts of cold and 2.5 parts of hot water. It is insoluble in alcohol and ether. By rapidly boiling the aqueous solution, lactose may be obtained in anhydrous crystals, which dissolve in 3 parts of cold water, but quickly deposit in the hydrated form.

Lactose is a much stronger reducing agent than sucrose, and precipitates cuprous oxide when gently treated with alkaline cupric solution; a fine mirror of silver is deposited when silver nitrate is mixed with ammonia, potash, and lactose, and gently warmed. Milk-sugar also differs from cane-sugar in becoming brown when heated with potash. When boiled with diluted acids, it undergoes hydrolysis like sucrose, yielding dextrose and *galactose* ($C_6H_{12}O_6$), isomeric with lævulose, but rotating the plane of polarisation of light to the right instead of the left. Yeast causes a similar change, subsequently fermenting the dextrose into alcohol (as in *koumiss*). Putrefaction-ferments, such as old cheese, ferment milk-sugar into lactic acid (see p. 513). It is unchanged by heating to 100° C. with solution of oxalic acid, which inverts sucrose. When oxidised by nitric acid, it yields mucic acid (see p. 527) and saccharic acid (p. 527). When acted on by water and sodium-amalgam, lactose yields mannite, $C_6H_{14}O_6$, dulcite, $C_6H_{14}O_6$, (iso)propyl alcohol, $C_3H_7.OH$, and (secondary) hexyl alcohol, $C_6H_{13}.OH$. In its behaviour with bases and with acetic anhydride, milk-sugar resembles cane-sugar.

Melitose, $C_{12}H_{22}O_{11}.3H_2O$, is the chief constituent of *Australian manna*, an exudation from *Eucalyptus mannifera*. It crystallises in fine needles, which lose 2 Aq at 100° C., and the third at 130°. It is but slightly sweet, and dissolves in water and alcohol. Melitose does not reduce alkaline cupric solution, and is dextrorotatory. Diluted acids and yeast convert it into dextrose and *eucalin*, $C_6H_{12}O_6$, an amorphous non-fermentable sugar which reduces alkaline cupric solutions.

Melezitose, $C_{12}H_{22}O_{11}.H_2O$, is extracted by alcohol from the manna exuding from the larch. It forms crystals which lose H_2O at 100° C., and are sweet enough to be used as a substitute for sugar. It does not easily reduce alkaline cupric solution, and is dextrorotatory. It is converted, though not easily, into dextrose by boiling with dilute acids.

Trehalose, or *mycose*, $C_{12}H_{22}O_{11}.2H_2O$, is found in the *trehala manna*, or *nest-sugar*, of Persia, an edible substance produced by an insect from the tree on which it lives. It is also found in the *ergot* of rye and in certain edible fungi, whence its name of mycose. Alcohol extracts it from the manna. It crystallises in prisms which have a sweet taste, and fuse at 100° C., losing their water at 130° C. It is soluble in water and in hot alcohol, but not in ether. In other respects it resembles the preceding.

Synanthrose, $C_{12}H_{22}O_{11}$, is found in the tubers of some plants of the Synantheraceous order (*Compositæ*), such as the dahlia and the Jerusalem artichoke, both belonging to the sub-order *Corymbiferæ*. It is an amorphous deliquescent substance, not sweet nor optically active. Acids and yeast resolve it into dextrose and lævulose.

Maltose, $C_{12}H_{22}O_{11}.H_2O$, is formed by the action of malt upon starch, and was formerly mistaken for glucose ($C_6H_{12}O_6$), but it is less soluble in alcohol, more dextrorotatory, and does not reduce a weak acetic solution of cupric acetate. To prepare maltose, starch (100 parts) is ground up with water (450 parts) and gelatinised by heating on a water-bath; after cooling, crushed malt (7 parts) is added, and the mixture kept at about 65° C. (149° F.) for an hour. The malt (germinated barley) contains an albuminoid substance termed *diastase*, which acts like a ferment upon the starch, causing it to undergo hydrolysis into maltose and dextrin—

$$3C_6H_{10}O_5\ (\textit{starch}) + H_2O = C_{12}H_{22}O_{11}\ (\textit{maltose}) + C_6H_{10}O_5\ (\textit{dextrin}).$$

The mixture, which has now become much more liquid, is boiled, filtered, evaporated to a syrup on the water-bath, and boiled with alcohol, which leaves the dextrin undissolved, and, on standing for some days, deposits the maltose in crusts of fine needles, which become anhydrous at 100° C. Maltose is easily fermented by yeast, yielding alcohol and carbon dioxide—

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

Boiling with dilute acids converts it into glucose—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

It reduces the alkaline cupric solution when warmed, but not the acetic solution.

530. *Glucose*, *dextrose*, or *grape-sugar*, $C_6H_{12}O_6$, is the crystallised sugar found in honey, raisins, and many other fruits; it is almost always accompanied by lævulose, which is far more difficult to crystallise, and is isomeric with it. Dextrose is also found in small quantity in several animal fluids, and in the liver, and it is abundant in urine in cases of *diabetes*.

Dextrose may be obtained from honey by mixing it with cold alcohol to dissolve the lævulose, which forms about one-third of its weight, and leaves about an equal quantity of dextrose, which may be dissolved in boiling alcohol and crystallised. To extract it from fruits, they are crushed with water, strained, the liquid boiled to coagulate albumen, filtered, evaporated to a syrup, and set aside for some days, when crystals of dextrose are deposited. Fresh fruits contain chiefly lævulose, which is gradually converted into dextrose.

Dextrose may be prepared from cane-sugar, by acting on it with an alcoholic solution of hydrochloric acid, and draining the solution of lævulose away from the crystals. 250 c.c. (or 9 fluid oz.) of alcohol (sp. gr. 0.823) are mixed with 10 c.c. (or 3 drachms) of strong hydrochloric acid; the mixture is heated to 45° C. (113° F.), and 80 grms. (or 1235 grains) of finely powdered cane-sugar added in small quantities. When the sugar has entirely dissolved, it is set aside for a week, stirred to induce crystallisation, the crystals drained on a filter and washed with alcohol.

Commercial glucose, or *starch-sugar*, is made by heating starch with diluted sulphuric acid, which first converts it into the isomeric dextrin, which combines with the elements of water to form dextrose—

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Water containing about 1.5 per cent. of sulphuric acid is heated to boiling, and a hot mixture of starch and water is allowed to flow gradually into it. The mixture is boiled for half an hour, neutralised with chalk, and concentrated by evaporation, when it deposits crystals of calcium sulphate. The clear syrup is drawn off and evaporated in a vacuum-pan

(p. 644) till it is strong enough to crystallise, which is accelerated by adding some glucose from a previous crystallisation. The glucose thus obtained contains maltose, dextrin, and some calcium-salts of organic acids; it may be purified by washing with strong alcohol mixed with 3 per cent. of HCl, and afterwards with commercial absolute alcohol.

Properties of glucose.—When crystallised from an aqueous solution, glucose forms six-sided scales, containing a molecule of water; these fuse at 86° C., and become anhydrous at 110° C.; it crystallises from alcohol in small needles, which are anhydrous. It is less sweet than sucrose. Glucose dissolves in 1.2 part of cold water, in 50 parts of cold alcohol (sp. gr. .837), and in 5 parts of boiling alcohol. When heated to 170° C., it is converted into *glucosan*, $C_6H_{10}O_5$, a nearly tasteless substance, convertible into glucose by dilute acids. When boiled with caustic potash, glucose gives a dark brown solution, which contains pyrocatechin (p. 635), together with potassium lactate and formate. In presence of alkalies, glucose acts as a strong reducing agent. If a solution of glucose be mixed with cupric sulphate, and potash be gradually added, the blue precipitate of cupric hydrate produced at first, dissolves in excess of potash to a fine blue solution; if this be gently heated, a yellow precipitate of cuprous hydrate is produced, which becomes red cuprous oxide when boiled; a little metallic copper is precipitated at the same time. Glucose precipitates metallic silver when warmed with ammonio-nitrate of silver, and metallic mercury from mercuric cyanide mixed with potash.

Solution of glucose mixed with sodium chloride deposits crystals of

$$2C_6H_{12}O_6.NaCl.H_2O,$$

which is sometimes deposited from diabetic urine. Glucose is not so easily blackened by sulphuric acid as sucrose, but forms an unstable combination with it.

In its behaviour with water and sodium-amalgam, dextrose resembles lactose, yielding mannite, ethyl, (secondary) propyl and hexyl alcohols, and lactic acid.

Dextrose resembles sucrose in its relations to basic oxides. When heated with acids of the acetic series, dextrose exchanges hydrogen for the acid radicals; thus, by heating it with glacial acetic acid to 100° C. for some hours, a very bitter liquid is obtained, which appears to be $C_6H_7(C_2H_3O)_5O_6$. When dextrose is heated with acetic anhydride, compounds are produced in which two and three atoms of hydrogen have been exchanged for acetyl (C_2H_3O). When heated with acetic anhydride and sodium acetate, it yields octaceto-diglucose, $C_{12}H_{14}(C_2H_3O)_8O_{11}$, which may be crystallised from ether, and yields *diglucose*, $C_{12}H_{22}O_{11}$, when decomposed by alkalies. Diglucose is isomeric with sucrose, but it forms an amorphous mass. It may also be obtained by passing HCl gas through an iced alcoholic solution of dextrose in the dark.

Dextrose rotates the plane of polarisation to the right hand, but a solution which has been kept for some hours has only half the effect of a freshly made solution. When glucose is oxidised by chlorine-water, it yields *gluconic acid*, which is isomeric with *mannitic acid*, $C_5H_6(OH)_5.CO_2H$, produced by the oxidising action of platinum black on mannite; if this last be represented as

$$C_5H_6(OH)_5.CH_2OH,$$

gluconic acid would be the corresponding acid, and dextrose might be regarded as the aldehyd, $C_5H_6(OH)_5COH$, a view supported by its strong reducing action. On the other hand, its behaviour with the fatty acids would indicate it to be a pentahydric alcohol, $C_6H_7O(OH)_5$. Nitric acid converts dextrose into saccharic acid, $C_4H_8O_4(CO_2H)_2$, and afterwards into *cassonic acid*, $C_3H_6O_3(CO_2H)_2$, and oxalic acid.

Acetyl chloride converts dextrose into $C_6H_7Cl(C_2H_3O)_4O_6$, which is converted by nitric acid into $C_6H_7NO_2(C_2H_3O)_4O_6$.

Glucose is much used by brewers and distillers for making alcohol, as well as by confectioners; dyers and calico-printers use it to reduce indigo.

531. *Fruit-sugar*, or *lævulose*, $C_6H_{12}O_6$, is prepared by heating cane-sugar with water and a very little sulphuric acid on a water-bath for

half an hour, removing the acid by barium carbonate, and evaporating to a syrup. This syrup contains *invert-sugar*, a mixture of equal weights of dextrose and lævulose (p. 643), which slowly deposits crystals of dextrose when exposed to light. To obtain pure lævulose, it is mixed with water, cooled in ice, and stirred with calcium hydrate, which precipitates a sparingly soluble lime compound of lævulose. This is suspended in water and decomposed by CO_2; the filtrate from the calcium carbonate is then evaporated on a water-bath. The syrup is washed with cold alcohol and set aside in a cold place, when the lævulose crystallises.

Lævulose is much sweeter than dextrose, rivalling cane-sugar in this respect. It does not ferment so readily as dextrose, so that when invert-sugar is mixed with yeast, the dextrose is the first to disappear. It also reduces alkaline cupric solutions less readily. When oxidised by chlorine or bromine water, it yields glycolic acid, $CH_3O.CO_2H$, while dextrose yields gluconic. Lævulose rotates the plane of polarisation of light to the left hand, whence its name. It forms two crystalline compounds with lime, $C_6H_{12}O_6.CaO.2Aq$ and $C_6H_{12}O_6.3CaO$, requiring, respectively, 137 and 333 parts of cold water for solution.

When heated to 170° C., lævulose is converted into lævulosan, $C_6H_{10}O_5$, which is dextrorotatory (p. 643).

Galactose, $C_6H_{12}O_6$ (formerly called lactose), is obtained, together with dextrose, when milk-sugar and some varieties of gum arabic are boiled with dilute sulphuric acid. To prepare it, milk-sugar is boiled for six hours with four parts of water containing 5 per cent. of sulphuric acid. The solution is precipitated by baryta, filtered, evaporated to a syrup, and induced to crystallise by adding a few crystals of dextrose. It is then washed with alcohol of 80 per cent., and recrystallised from hot alcohol of 70 per cent. It crystallises in rhombic prisms, which are less sweet than cane-sugar. It is not very soluble in cold water, and is insoluble in absolute alcohol. Galactose is more strongly dextrorotatory than dextrose, and resembles it in its reducing action on copper and silver salts; it is not easily fermented. Nitric acid converts it into mucic acid, $C_4H_8O_4(CO_2H)_2$, as it does lactose; and they both yield *lactonic acid*, $C_5H_9O_4.CO_2H$, when oxidised by bromine-water. Sodium-amalgam and water reduce it to *dulcite*, $C_6H_8(OH)_6$, isomeric with mannite (p. 646).

Arabinose, $C_6H_{12}O_6$, is produced by boiling some kinds of gum arabic with dilute sulphuric acid, being formed from *arabin*, $C_{12}H_{22}O_{11}$. It is very sweet, and even more dextrorotatory than galactose. It reduces alkaline cupric solution, and is oxidised by nitric acid to oxalic acid. Some kinds of gum arabic yield galactose when boiled with sulphuric acid, but these may be distinguished by oxidising with nitric acid, when they yield mucic acid.

532. *Inosite*, or *flesh-sugar*, $C_6H_{12}O_6.2H_2O$, is obtained from the juice of beef; the chopped heart or lung of the ox is exhausted with water, the liquid pressed out, mixed with a little acetic acid, and heated to boiling. The liquid filtered from the coagulated albumen is mixed with lead acetate, filtered, and basic lead acetate added; this precipitates a lead compound of inosite, $2C_6H_{12}O_6.5PbO$, which is to be suspended in water and decomposed by H_2S, when the inosite passes into solution. The lead sulphide is filtered off, the solution evaporated on the water-bath to a syrup, and mixed with ten volumes of alcohol and one of ether, when the inosite is precipitated. It forms prismatic crystals, which are sweet and soluble in 6 parts of cold water. It is but slightly soluble in weak alcohol, and insoluble in absolute alcohol and in ether. The crystals effloresce in air, and become anhydrous at 100° C. Inosite differs from glucose in not giving a brown colour with potash, or reducing alkaline cupric solution, even after boiling with dilute sulphuric acid. It is not fer-

mented by yeast, but animal-ferments, such as decaying cheese, convert it into lactic, butyric and carbonic acids. Nitric acid oxidises it to oxalic acid. It is optically inactive. Inosite may be identified by moistening it with dilute nitric acid, evaporating almost to dryness, and adding ammoniacal calcium chloride, which produces a rose colour. Inosite solution mixed with a drop of mercuric nitrate gives a yellow precipitate, which becomes red when heated.

The proportion of inosite obtained from flesh is very small; many vegetables contain it more abundantly. The unripe French bean yields 0.75 per cent. of inosite; walnut-leaves, in August, 0.3 per cent. It is also present in the leaves of ash and vine; grapes contain it, so that inosite is found in wine. Unripe peas, asparagus, and dandelion contain inosite. It may be extracted from vegetables by exhausting them with water, neutralising the acid liquid with baryta, and treating with lead acetate as in the case of flesh.

Inosite has been found in the urine in cases of Bright's disease.

The absence of reducing-power in inosite indicates that it is not an aldehyd-sugar, but an alcohol. When it is dissolved in strong nitric acid, and strong sulphuric acid added, a precipitate of $C_6H_6(NO_3)_6$ is obtained, which may be crystallised from alcohol in explosive prisms, the mother liquor from which yields needles of $C_6H_6(OH)_3(NO_3)_3$. This suggests that inosite is a hexhydric alcohol, $C_6H_6(OH)_6$.

Scyllite, $C_6H_{12}O_6$, is obtained from the liver of the dog-fish (*Scyllium*), skate, and shark. It much resembles inosite, but is less soluble in water, and yields anhydrous crystals.

Dambose, $C_6H_{12}O_6$, is so called from the native name for caoutchouc, which, when exhausted with alcohol, yields a volatile crystalline body, *dambosite*, $C_6H_{10}(CH_3)_2O_6$, which yields dambose and methyl chloride when decomposed by HCl. Dambose forms prismatic crystals, soluble in water but not in alcohol. *Borneo dambose*, $C_6H_{12}O_6$, is obtained by the action of hydriodic acid on *bornesite*, $C_6H_{11}(CH_3)O_6$, methyl iodide being also formed. Bornesite is extracted by alcohol from Borneo caoutchouc.

533. *Summary of the principal sugars.*—The *sucroses*, or *saccharoses*, when dried, all have the composition, $C_{12}H_{22}O_{11}$.

They all rotate the plane of polarisation of light towards the right hand.

They dissolve in absolute alcohol, *except cane-sugar* and *milk-sugar*.

They do not reduce alkaline cupric solution, *except milk-sugar* and *maltose*.

They are not *directly* fermented to alcohol by yeast, *except maltose*.

The *glucoses*, when dried, all have the composition $C_6H_{12}O_6$.

They all rotate the plane of polarisation towards the right, *except fruit-sugar*, which is lævorotatory, and *inosite*, which is inactive.

They dissolve in absolute alcohol, *except galactose* and *inosite*.

They reduce alkaline cupric solution, *except inosite*.

They are not *directly* fermented to alcohol, *except grape-sugar* and *fruit-sugar*.

534. STARCH, or *amylose*, $C_6H_{10}O_5$, differs from the sugars in being insoluble in cold water, and therefore tasteless, and in not forming crystals, but having an *organised* structure visible under the microscope, which is not seen in any artificial product of the laboratory. It is an indispensable constituent of all plants (except fungi), and is stored up in their seeds and tubers, for the nourishment of the young shoots.

To obtain starch on the small scale, flour (which contains about 60 per cent.) is mixed with cold water to a stiff *dough*, which is tied up in fine muslin, and well kneaded in a basin of distilled water, when the grains of starch pass through, leaving the tenacious *gluten* in the muslin. The milky fluid is allowed to settle for a few hours, the greater part of the water poured off, the starch collected on a filter, and dried by exposure to air.

On the large scale, in England, starch is commonly made from rice, which contains about 80 per cent. The rice is soaked for 24 hours in water containing about 0.3 per cent. of caustic soda; it is then washed and ground into flour, which is again soaked for two or three days in a fresh alkaline solution; the starch is allowed to settle, and the alkaline liquid, holding the gluten in solution, is drawn off. The starch is then stirred up with water, the heavier woody fibre allowed to subside, and the milky liquid is run off into another vessel, where it deposits the starch. This is transferred to drainers, where it is allowed to get partly dry, and the drying is finished by gradual application of heat, when it splits into roughly prismatic fragments, which still retain about 18 per cent. of water. Commercial starch is generally coloured blue by a little ultramarine or smalt, in order to correct the yellow tint of linen.

Properties of starch.—Being possessed of an organised structure, starch varies in external aspect, according to the plant from which it is obtained. When powdered starch is examined by the microscope, it appears in grains resembling some of those in fig. 285, the largest grains being those of potato-starch (P), about $\frac{1}{300}$ inch in the longest diameter; the smallest are those of rice (R), about $\frac{1}{3000}$ inch in diameter; wheat starch (W) has nearly spherical granules, $\frac{1}{1000}$ inch in diameter; (A) is the starch of *arrowroot*, from *Maranta arundinacea*, a tropical plant. When moistened with water and viewed under a microscope provided with a polariser and analyser, starch granules behave like doubly refracting crystals, exhibiting a black cross when the planes of polarisation of the polariser and analyser are at right angles, which becomes white when the analyser is turned through an angle of 90°; this is best seen in the starch of potato, Indian corn, and *tous les mois* (from *Canna coccinea* of the Arrowroot order). The starch granules are composed externally of *starch-cellulose*, or *farinose*, and internally of *granulose*, and, perhaps, other isomeric bodies.

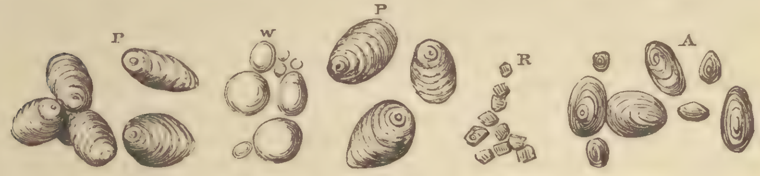


Fig. 285.

Cold water does not act on starch, unless the cell-walls are broken by trituration, when a part of the granulose dissolves, yielding a solution which is strongly dextrorotatory and is coloured blue by iodine, which gives a violet colour to farinose. When starch is heated with water to about 50° C. (122° F.), the granules begin to burst, which is completed at about 70° C. (158° F.), when the granulose is dissolved to a viscous liquid, which becomes a jelly on cooling, and a gummy mass when dried. The cell-wall may be dissolved in the cold by strong alkalies, acids, and zinc chloride. When starch is heated with glycerin to 190° C. (374° F.), it is dissolved, and if the solution be mixed with alcohol, *soluble starch* is precipitated, and, while moist, may be dissolved by water or weak alcohol. Its strong aqueous solution becomes a jelly on standing.

The aqueous solution of starch is precipitated by alcohol, by baryta, and lime, and by ammoniacal lead acetate, which gives $C_6H_{10}O_5.PbO$. For the behaviour of starch with iodine, see p. 175. When boiled with diluted sulphuric or hydrochloric acid, starch is converted into maltose and dextrin (p. 647). Concentrated nitric acid dissolves starch in the cold, and if the solution be poured into water, it precipitates *xyloidin*, an explosive compound, which is a mixture of $C_{12}H_{19}O_9(NO_3)$ and $C_{12}H_{18}O_8(NO_3)_2$. If a mixture of nitric and sulphuric acids be used, the compound $C_{12}H_{16}O_6(NO_3)_4$ is obtained. The existence of these compounds suggests that starch should be represented by the formula $C_{12}H_{16}O_6(HO)_4$. They may be reconverted into starch by reduction with ferrous chloride and iron filings.

When starch is heated with acetic anhydride, it yields an insoluble compound, which may be represented as $C_{12}H_{14}O_4(C_2H_3O_2)_6$. It yields starch and potassium acetate when saponified by potash; this represents starch to be a hexhydric alcohol, $C_{12}H_{14}O_4(HO)_6$. Strong sulphuric acid dissolves starch in the cold, apparently forming a soluble sulpho-acid. When heated, carbonisation takes place.

Starch may be converted into cane-sugar by digesting it with dilute sulphuric acid at 100° C. and passing an electric current through the solution until it is no longer coloured by iodine.

When starch is heated to about 205° C. (400° F.) for some hours, it acquires a brownish colour and becomes soluble in cold water, having been converted into the isomeric compound dextrin. This conversion of starch into a soluble form is important in the preparation of food. In toasting bread a portion of the starch is converted into dextrin, which is dissolved in toast and water. When further heated, starch is carbonised and yields products of destructive distillation resembling those from sugar.

535. *Dextrin*, or *British gum*, $C_6H_{10}O_5$, is prepared by moistening starch with one-third of its weight of weak nitric acid (0.66 per cent.), drying it in air, and heating to 115° C. (240° F.).

There are two varieties of dextrin—viz., *erythro-dextrin*, which is coloured red by iodine water; and *achro-dextrin*, which is not coloured. The erythro-dextrin is formed at first when starch is boiled with diluted sulphuric acid, so that the blue starch-reaction with iodine gives place to a red, and finally ceases. Commercial dextrin gives a violet colour with iodine, because it contains unaltered starch and erythro-dextrin; it is sweet from the presence of glucose. It may be purified by dissolving in water and precipitating by alcohol.

Dextrin dissolves when soaked in water, and is left on evaporation as a transparent mass. Its solution has twice the dextrorotatory power of dextrose. Pure dextrin does not reduce alkaline cupric solution; but commercial dextrin does so, though not so quickly as glucose. When boiled with dilute sulphuric, or hydrochloric acid, it is converted into dextrose. Nitric acid oxidises it to oxalic acid, while ordinary gum yields mucic acid. Heated with acetic anhydride, it yields an acetyl-compound isomeric with that obtained from starch (see above), which is converted into the dextrin-derivative by heating to 160° C. Dextrin is used by calico-printers for thickening their colours; it is used for adhesive stamps, for confectionery, and for stiffening surgical bandages.

Inulin, $(C_6H_{10}O_5)_6.H_2O$, was first obtained from elecampane root (*Inula helenium*), an aromatic medicinal plant. It is also found in the roots of the dahlia, and in the Jerusalem artichoke, which belong to the same sub-order (*Corymbiferæ*), and in the roots of dandelion and chicory, belonging to the *Cichoraceæ*; all being plants of the natural order *Compositæ*. It may be extracted from dahlia roots, which contain 10 per cent., by boiling with water, which deposits the inulin on cooling. It is not coloured blue by iodine, and does not reduce alkaline cupric solution. It is insoluble in alcohol. Solution of inulin is lævorotatory. When boiled with dilute sulphuric acid, it yields lævulose. It also differs from starch in being unchanged by diastase.

Glycogen, or *animal starch*, $C_6H_{10}O_5$, occurs in the liver, in blood, and in flesh, also in yolk of egg, and in oysters, where it is said to amount to 9.5 per cent. of the dried fish. It is most abundant in the liver during active digestion, and disappears quickly after death, being converted into dextrose by fermentation. To prepare glycogen, the minced liver is extracted with water as long as it runs off milky; the albumen is coagulated by boiling, and the filtrate mixed with alcohol, which precipitates the glycogen; it is purified by boiling with weak acetic acid to remove albuminoid bodies, again precipitating with alcohol, and washing with ether to remove traces of fat. When dried over calcium chloride, glycogen has the formula $(C_6H_{10}O_5)_2.H_2O$, and it loses the H_2O at 100° C. It it an amorphous powder like starch, swelling in water, and yielding a turbid solution on heating. The solution is strongly dextrorotatory, and gives a wine-red colour with iodine. Glycogen does not reduce alkaline copper solution, and is not fermented by yeast. Diastase converts it into maltose and dextrin, as it does starch (p. 647). It is converted into dextrose when boiled with dilute sulphuric or hydrochloric acid, or when placed in contact with saliva or pancreatic juice.

536. GUMS.—The carbohydrates of this group resemble dextrin in yielding viscous solutions in water, in being precipitated by alcohol, and in conversion into sugars by boiling with dilute acids: but the gums have a marked acid tendency, though they do not form well-defined salts. Moreover, the gums yield mucic acid when oxidised by nitric acid.

Arabin, or *Arabic acid*, $C_{12}H_{22}O_{11}$, occurs in *gum-arabic*, an exudation from various tropical acacias. It is extracted by dissolving the gum in water, acidulating with HCl, and adding alcohol, which precipitates it in white flakes; or the acid solution may be dialysed (p. 114), when the aqueous solution of arabin remains in the dialyser. The pure aqueous solution is not precipitated by alcohol, but the presence of a minute quantity of a base or a salt determines the precipitation. The aqueous solution has an acid reaction, and, on evaporation, leaves a vitreous mass, which loses water above 120° C., yielding *metarabin* isomeric with dextrin. This does not dissolve in water, but increases greatly in bulk. Arabic acid decomposes alkaline carbonates, and the composition of its salts indicates the formula $C_{36}H_{66}O_{33}$ or $H_2C_{36}H_{64}O_{33}$. It appears to occur in gum-arabic as arabates of calcium, magnesium, and potassium, since, when incinerated, the gum leaves about 3 per cent. of ash containing those metals. Arabin gives a characteristic reaction with cupric sulphate, followed by potash, which produces a blue precipitate, insoluble in excess, and neither blackened nor reduced by boiling, but collecting into a blue mass, leaving the liquid colourless. If this mass be dissolved in HCl, and boiled for a short time, excess of potash gives a clear blue solution, which deposits much red cuprous oxide when boiled. When arabin is boiled with dilute sulphuric acid it is converted into *arabinose*, or *gum-sugar*, $C_6H_{12}O_6$, which is very sweet, strongly dextrorotatory, and reduces alkaline cupric solution, but is not fermentable; it may be crystallised. Dextrose is formed at the same time.

Gum Senegal, obtained from similar sources, is used by calico-printers to thicken their colours. It is darker in colour than gum arabic, but also consists essentially of arabin.

Metarabin, or *cerasin*, $C_{12}H_{20}O_{10}$, is found in the gum of the cherry-tree, probably as calcium metarabate, which remains undissolved after the calcium arabate which accompanies it has been extracted by water; when heated with lime-water, it is converted into calcium arabate, which dissolves. It is also found in the residue of beet-root from which the juice has been expressed.

Bassorin, very similar to cerasin, occurs in *Bassora gum* and in *gum tragacanth*, the exudation from *Astragalus tragacantha*, a Papilionaceous plant. These gums do not dissolve in water like gum arabic, but swell up immensely by absorption of water, and form a *mucilage*. When boiled with dilute acids it is converted into dextrose. A substance very similar to bassorin is formed in the *ropy* or *viscous fermentation* of saccharine liquids. The mucilaginous liquids obtained by boiling linseed (*linseed tea*), quince-seed, and marshmallow root with water, contain bassorin, or some allied body.

Gelose, or *parabin*, $C_{12}H_{22}O_{11}$, forms the greater part of Ceylon moss (*Gracilaria lichenoides*) and China moss (*G. spinosa*), sea-weeds, which are used for making soups and jellies. Carrots and beet also contain gelose. When dissolved in as much as 500 parts of hot water, it sets to a jelly on cooling. It also differs from the other bodies of this group by dissolving in dilute acids, and being precipitated by alkalies. When long heated with alkalies it is converted into arabin. It does not appear to yield a sugar when boiled with dilute acids.

537. CELLULOSE, $C_6H_{10}O_5$, is the substance which composes the walls of plant cells, and is left undissolved after the matters contained in and encrusting the cells have been removed by various solvents. Hence, white filter-paper, prepared cotton-wool, and well-washed linen consist of nearly pure cellulose.

Preparation of cellulose.—Sawdust is dried at 110° C. and boiled with a mixture of alcohol and benzene to extract resinous matters. It is then washed with alcohol, and boiled two or three times with very weak ammonia, after which it is washed and digested with weak bromine-water (0.4 per cent.) until it no longer decolorises the bromine-water after 24 hours. This oxidises the *vasculose* (formerly called lignin), and converts it into acids. The residue is washed, and heated nearly to boiling with water containing $\frac{1}{250}$th part of its volume of strong ammonia; this dissolves the oxidised acids, and acquires a brown colour. When this no longer increases, the residue is again washed, and the treatment with bromine-water repeated until no more brown colour is imparted to the ammonia; a final washing with water and boiling with alcohol leave the cellulose pure.

Properties of cellulose.—When pure, cellulose is white, opaque, exhibits an organised structure, is infusible and insoluble in all ordinary solvents. It may be dissolved by *Schweitzer's reagent*, which is made by dissolving cupric hydrate (p. 380) in ammonia. The cellulose is reprecipitated in flakes on addition of an acid. When cellulose is subjected to destructive distillation it yields formic, acetic, propionic, and butyric acids, but no methyl alcohol (which is derived from the vasculose in wood). When distilled with manganese dioxide and sulphuric acid, it yields formic acid. Chlorine, in presence of moisture, slowly acts upon cellulose, so that paper becomes brittle if the excess of bleach be not *killed* by an antichlore (p. 200). Iodine does not give a blue colour with pure cellulose, but the cellular tissue of plants is often blued by it, from the presence of a little starch. Ferric oxide slowly oxidises cellulose, and, since the ferrous oxide is repeatedly oxidised again, a continual oxidation and corrosion of the cellulose is kept up, as may be seen from the effect of *iron-mould* on linen and of rusty nails on wood.

Strong sulphuric acid converts dry cellulose into a gummy mass which dissolves in the acid with very little colour in the cold. If this solution be immediately poured into water, it yields a gelatinous precipitate, but after digestion for some hours with the acid, a clear solution is formed in water, and if this be largely diluted and boiled, the cellulose is converted, first into dextrin, and then into dextrose, which may be obtained as a syrup by neutralising the acid liquid with chalk, filtering, and evaporating. By fermenting this dextrose, the curious transformation of rags into alcohol may be accomplished. Cotton wool dissolves in a mixture of sulphuric acid with one-fourth its weight of water, and, on dilution, a precipitate of *amyloid* is obtained, which is isomeric with cellulose, but is coloured a fugitive blue by iodine.

By immersing unsized paper in a cold mixture of strong sulphuric acid with half its volume of water, it becomes converted externally into amyloid. This is turned to account for making *vegetable parchment*, which is five times as strong as paper, and is waterproof. After immersion in the acid, the paper is thoroughly washed with water and finally with weak ammonia. A strong solution of zinc chloride affects the paper in the same way. The *parchment paper* is translucent; it may be boiled in water without disintegration; it receives many useful applications, as for luggage labels which are not easily torn or destroyed by rain, as a substitute for bladder in tying over preserves, &c., and for making dialysers.

When cellulose is left for twelve hours in sulphuric acid of sp. gr. 1.453, or in hydrochloric acid of sp. gr. 1.16, it is converted into a brittle mass of *hydrocellulose*, $C_{12}H_{22}O_{11}$, which is more easily oxidised than cellulose, and dissolves in hot potash. This is applied for dissolving the cotton from old fabrics containing wool, the latter being left as *shoddy*. *Dry rot* is ascribed to a similar change in the wood caused by acid substances generated in its fermentation.

Cellulose swells up and becomes gummy when in contact with strong potash or soda; on heating to 160° C. with strong potash, it dissolves, and the solution, when acidified, yields a precipitate isomeric with cellulose, but easily soluble in alkalies. If calico be soaked for half an hour in very strong potash or soda, and washed with alcohol, it is converted into $C_{12}H_{20}K_2O_{11}$, or $C_{12}H_{20}Na_2O_{11}$. Both compounds are decomposed by carbonic acid. When cellulose is boiled with potash of sp. gr. 1.5, it dissolves with a brown colour, and the solution deposits brown flakes (*ulmic acid*) when acidulated; but on prolonged heating, the colour disappears, and carbonate, oxalate, formate, and acetate of potassium are found in solution. By fusing cellulose with potash, abundance of potassium oxalate is obtained (see *Oxalic acid*).

If it be heated to 200° C. with potash and a little water, it evolves hydrogen and methyl alcohol, leaving potassium carbonate, oxalate, acetate, and propionate.

When heated with strong ammonia to 150° C., cellulose is slowly converted into a brown gummy deliquescent mass of a bitter taste.

For the detection of cellulose in the microscopic examination of tissues, advantage is taken of its conversion into amyloid by zinc chloride, and of the bluing of this by iodine. The reagent is prepared by dissolving six per cent. of potassium iodide in solution of zinc chloride of sp. gr. 1.8, and adding as much iodine as it will dissolve.

By heating cellulose with 8 parts of acetic anhydride in a sealed tube to 180° C., it may be converted into *tri-acetyl cellulose*—

$$C_6H_{10}O_5 + 3(C_2H_3O)_2O = C_6H_7O_2(O.C_2H_3O)_3 + 3(HO.C_2H_3O).$$

The new compound remains dissolved in the acetic acid, and is precipitated on adding water, in white flakes which are insoluble in alcohol and ether. This reaction of cellulose might allow it to be regarded as a tri-hydric alcohol, $C_6H_7O_2(OH)_3$.

538. *Action of nitric acid on cellulose.*—Cold dilute nitric acid (sp. gr. 1.2) does not act on cellulose in the form of filter paper, and scarcely when heated to 100° C. Acid of 1.42 corrodes it, producing amyloid and malic acid, and, on boiling, suberic and oxalic acids. Cotton, linen, or paper, soaked for two or three minutes in the strongest nitric acid and washed, resembles parchment, and is waterproof and very combustible, having become partly converted into *cellulo-trinitrin*, or *pyroxylin*; $C_6H_7O_2(OH)_3 + 3(HO.NO_2) = C_6H_7O_2(O.NO_2)_3 + 3HOH$. This change, which is analogous to the conversion of alcohol into the ethereal salts, is, like that conversion, much facilitated by the presence of strong sulphuric acid, which may either act simply as a dehydrating agent or may form an intermediate sulphonic acid.

If pure dry cellulose (prepared cotton wool) be steeped for some time in a cold mixture of equal molecular weights of the strongest nitric and sulphuric acids, and afterwards thoroughly washed, and dried by exposure to air, it has the composition of cellulotrinitrin above given, retaining the organised structure of the original cotton, but being somewhat harsher to the touch, and becoming highly electrified when drawn through the dry hand.

Cellulotrinitrin is insoluble in water, alcohol, and ether, either separately or mixed, but it dissolves in acetic ether and in ethereal solution of ammonia. It is not oxidised by potassium permanganate, as cellulose is, so that it may be used for filtering its solution. When moderately heated, it burns more rapidly than gunpowder, and it is detonated by the blow of a hammer or by the rapid vibration caused by a smart detonation in its vicinity. Pyroxylin dissolves in strong sulphuric acid, and the solution is not blackened by heat. Strong nitric acid also dissolves it when heated, but it is reprecipitated by strong sulphuric acid or by water. Strong potash dissolves it with formation of potassium nitrate, nitrite, and oxalate, together with glucose and some other organic bodies. The formation of potassium nitrate would be expected if pyroxylin be a nitric ether of cellulose.

Potassium hydrosulphide, in alcoholic solution, reconverts pyroxylin into cellulose, potassium nitrite being found in solution—

$$C_6H_7O_2(O.NO_2)_3 + 3KHS = C_6H_7O_2(OH)_3 + 3KNO_2 + S_3.$$

This shows that pyroxylin is not, as was formerly supposed, the *trinitrocellulose*, $C_6H_7(NO_2)_3O_5$, since, in that case, the NO_2 group would be reduced to the NH_2 group, and an amido-compound would be formed (p. 579).

A strong aqueous solution of ferrous chloride containing HCl also converts pyroxylin into cellulose, with evolution of nitric oxide—

$$C_6H_7O_2(O.NO_2)_3 + 6FeCl_2 + 6HCl = C_6H_7O_2(OH)_3 + 3Fe_2Cl_6 + 3NO + 3H_2O.$$

This would be the result expected from cellulose trinitrate. Iron filings and acetic acid reduce pyroxylin to cellulose, the nascent hydrogen converting the NO_3 group into NH_3—

$$C_6H_7O_2(NO_3)_3 + H_{24} = C_6H_7O_2(OH)_3 + 3NH_3 + 6H_2O.$$

Pyroxylin behaves like a nitrate when shaken with mercury and strong sulphuric acid, evolving the whole of its nitrogen as nitric oxide.

539. The following proportions may be recommended for preparation of guncotton on a small scale:—Dry 1000 grains of pure nitre (page 455) at a very

moderate heat, place it in a dry retort (fig. 286), pour upon it 10 drachms (by measure) of strong sulphuric acid, and distil until 6 drachms of nitric acid have passed over into the receiver. Dry some pure cotton-wool, and weigh out 30 grains of it. Mix 2½ measured drachms of the nitric acid with an equal volume of strong sulphuric acid in a small beaker. Allow the mixture to cool, immerse the cotton-wool in separate tufts, pressing it down with a glass rod, cover the beaker with a glass plate, and set it aside for fifteen minutes. Lift the cotton out with a glass rod, throw it into at least a pint of water, and wash it thoroughly in a stream of water till it no longer tastes acid or reddens blue litmus-paper. Dry the cotton by exposure to air or to a very moderate heat.

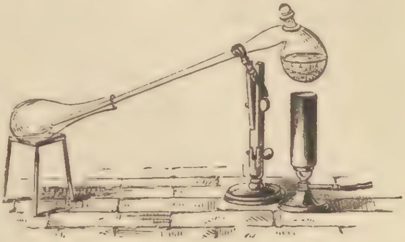


Fig. 286.

Very great attention has been paid to the manufacture of gun-cotton during the last few years, with the object of producing a perfectly uniform product which might be employed as a substitute for gunpowder.

The following is an outline of the process now generally adopted for the production of large quantities of gun-cotton by Abel's process:—

Manufacture of gun-cotton.—The cotton is employed in the form of the waste cuttings from spinning machines (cotton waste), and is thoroughly cleansed.

The proportions in which it is found most advantageous to mix the nitric and sulphuric acids are 1 part of nitric acid (sp. gr. 1.52) and 3 parts by weight (or 2.45 by volume) of sulphuric acid (sp. gr. 1.84). These proportions of the acids are placed in separate stoneware cisterns with taps, and allowed to run simultaneously, in slow streams, into another stoneware cistern furnished with a tap and an iron lid, through a second opening in which an iron stirrer is employed to mix the acids thoroughly. The mixture is set aside for several hours to become perfectly cool.

A quantity of the mixed acids is drawn off into a deep stoneware pan standing in cold water, and provided with a perforated iron shelf, upon which the cotton may be drained. The well-dried cotton is immersed, a little at a time, in the acid, and stirred about in it for two or three minutes with an iron stirrer. It is then placed upon the perforated shelf, and the excess of acid squeezed out with the stirrer. Enough acid is drawn from the cistern to replace that which has been absorbed by the cotton, and more cotton is treated in the same way. Since a considerable rise of temperature is produced by the action of the nitric acid upon the cotton, it is necessary to keep the pan surrounded with cold water. A large proportion of the cotton is doubtless converted into gun-cotton in this preliminary immersion in the mixed acids; but in order to convert the remainder, it is necessary to allow the cotton to remain in contact with the acid for a much longer period, so as to insure its penetration into every part of the minute twisted tubes of the fibre. The preliminary immersion of each skein has the advantage of wetting every part with the acid, which could not be so certainly effected if several skeins were thrown at once into a jar, and of preventing the great accumulation of heat which would ensue if the entire chemical action were allowed to take place upon a number of skeins at the same time. The amount of heat evolved during the subsequent soaking in acid is comparatively small.

The skeins are next transferred to a jar with a well-fitting cover, in which they are pressed down and completely covered with the mixed acids, of which from 10 to 15 times the weight of the cotton will be required, according to the closeness with which the skeins are packed in the jar. The jar is placed in cold water, and the cotton allowed to remain in the acid for about twelve hours.

The skeins are then removed, with the aid of an iron hook, to a centrifugal extractor, which is a cylinder made of iron gauze, through which the liquid is whirled out by the rapid rotation of the cylinder upon an axle. In this they are whirled, at first slowly, and afterwards at 800 revolutions per minute, during ten minutes, when the bulk of the acid is separated. In order to wash away the remainder of the acid, the cotton is plunged, suddenly, into a cascade of water; for if the water were allowed to come slowly into contact with the mixed acids, so much heat would be evolved as to decompose a portion of the pyroxylin. The cotton is then drained in the centrifrugal extractor, and again rinsed in much water. After two or three rinsings it is reduced to pulp in a rag-engine such as is employed in paper-mills. The pulp is thoroughly washed by being well stirred by a *poaching-engine* for about forty-eight hours in a stream of warm water, so as to remove every trace of acid, which is assisted by rendering the water alkaline with a little lime or carbonate of soda or with ammonia. The pulp is then drained, moulded into discs or any other required form, condensed by hydraulic pressure until it has at least the same specific gravity as water, and dried upon heated plates. As it leaves the hydraulic press, the cotton contains about one-fifth of its weight of water, so that it may, if required, be cut up or bored without danger of explosion.

The finished gun-cotton is examined by the following tests:—

1. Four grains are heated in a test-tube placed in an oil-bath, and containing a slip of moistened paper imbued with potassium iodide and starch (to detect nitrous vapours). No tinge should be imparted to the paper till the temperature of the oil reaches 190° F. (88° C.).

2. The experiment is repeated, omitting the test-paper, and closing the tube with a disc of card. No brown fumes should be perceived on looking down the axis of the tube below a temperature of 320° F. (160° C.).

3. One grain is heated in a test-tube placed in an oil-bath till it explodes, which should not happen below 343° F. (173° C.).

4. The gun-cotton should dissolve entirely in acetic ether, which would leave any unconverted cotton undissolved.

5. Fifty grains of the gun-cotton should suffer little loss in weight when digested for two or three hours with four ounces of a mixture of one volume alcohol and 2 volumes ether, which would dissolve any collodion-cotton.

540. *Products of the explosion of gun-cotton.*—From what has been stated with respect to the products of explosion of gunpowder (page 449), it might be expected that those furnished by gun-cotton would vary according to the conditions under which the explosion takes place. When a mass of the gun-cotton wool is exploded in an unconfined state, the explosion is comparatively slow (though appearing to the eye almost instantaneous), since each particle is fired by the flame of that immediately adjoining it, the heated gas (or flame) escaping outwards, so that some time elapses before the interior of the mass is ignited. But when the gun-cotton is enclosed in a strong case, so that the flame from the portion first ignited is unable to escape outwards, and must spread into the interior of the mass, this is ignited simultaneously at a great number of points, and the decomposition takes place far more rapidly; a given weight of cotton being thus consumed in a much shorter time, a far higher temperature is produced, and the ultimate results of the explosion are much less complex, as would be expected from the well-known simplifying effect of high temperatures upon chemical compounds.

If a tuft of gun-cotton wool be placed at the bottom of a tall glass cylinder, and inflamed by a heated wire, it will be seen that, immediately after the explosion, the gas within the cylinder is colourless, but it soon becomes red, showing that nitric oxide was present among the products, and became converted into nitric peroxide by the oxygen of the air. The water formed by the combustion of the hydrogen converts the nitric peroxide into nitrous and nitric acids (p. 145), and hence the acid character of the moisture deposited in the barrel of a fowling-piece in which gun-cotton cartridges are employed.

A little hydrocyanic acid can be detected among the products of combustion of loose gun-cotton.

Sarrau and Vieille, employing a gun-cotton containing 3 parts of cellulo-trinitrine and 1 part of cellulo-dinitrine, $C_6H_7O_2.OH.(NO_3)_2$, obtained, per gramme of gun-cotton—

Carbonic oxide	234 cub. cent.
Carbon dioxide	234 ,,
Hydrogen	166 ,,
Nitrogen	107 ,,
Total	741 ,,

At low pressures, steam was also produced, together with more carbonic oxide and less carbon dioxide.

Berthelot estimates the pressure produced by the detonation of gun-cotton, compressed to a density of 1.1, at 24,000 atmospheres, or about 160 tons per square inch, being only half the pressure assigned by him to the detonation of mercuric fulminate.

The experiments hitherto made have been unfavourable to the employment of gun-cotton as a substitute for gunpowder in artillery, on account of the injury which its violent explosion occasionally inflicts upon the gun. For use in fowling-pieces, the gun-cotton pulp is diluted with a proportion of ordinary cotton pulp, and made into a kind of paper which is rolled up to form the cartridges. Although such cartridges leave a considerable carbonaceous residue when fired on a plate, they leave little or no residue when fired under pressure.

If a piece of compressed gun-cotton be kindled with a hot wire, it burns rapidly away, producing a large volume of flame, but without any explosive effect.* In order that gun-cotton fired in this manner might be used for destructive purposes, it was found necessary to confine it in strong cases, so that the flame of the portion first ignited should be employed in raising the temperature of the rest to the exploding point.

The discovery, made by E. O. Brown, of a method by which the *unconfined* gun-cotton could be made to explode with most destructive violence, has opened a new career to this material, rendering it far superior to gunpowder for all blasting operations, torpedoes, &c. It is only necessary to explode in contact with the compressed cotton a *detonating fuze*, consisting of a little tube of quill or thin metal charged with a few grains of mercuric fulminate, to cause the cotton to detonate with extreme violence; and such detonation can be communicated along a row of pieces of compressed cotton placed at short distances from each other.

This capability of undergoing what may be termed *sympathetic explosion* is by no means confined to gun-cotton. Previously to Brown's discovery, Nobel had shown it to exist in the case of nitroglycerin, and Abel afterwards proved that most explosives, including even gunpowder, can be made to detonate in a similar manner. The *modus operandi* of the detonating fuze appears, from the experiments of Abel, as well as from those of Champion and Pellet, to consist in the influence of vibratory motion, and the nature of the motion necessarily depends upon the nature of the explosive. That it is not a result of the action of heat is proved by the circumstance that wet gun-cotton may be exploded by a detonating fuze, so that torpedoes may be charged with a mixture of gun-cotton pulp and water, containing 15 per cent. of the latter, if a small charge of dry gun-cotton be placed in contact with the fuze. It has been found that the wet gun-cotton is more easily detonated when in a frozen state.

The very destructive effect of the gun-cotton exploded in this way is, of course, due to the sudden manner in which the whole mass is resolved into gaseous products. When heat is the cause of the explosion, it must be comparatively slow, for gun-cotton transmits heat slowly, but the vibration caused by detonation is transmitted with the velocity of sound, and the explosion becomes rapid in proportion.

541. *Properties of gun-cotton compared with those of gunpowder.*—Gun-cotton is more easily exploded than gunpowder; the latter requires a temperature of at least 600° F. (316° C.), whilst gun-cotton may explode at 277° F. (136° C.), and must explode at 400° F. (204° C.). It is very difficult to explode gunpowder by percussion, even between a steel hammer and anvil; but gun-cotton invariably detonates in this way, though the explosion is confined to the part under the hammer. The explosion of gun-cotton is, of course, unattended by any smoke, a most important advantage in mines, the atmosphere of which is sometimes rendered almost intolerable by the smoke of gunpowder used in blasting, but death has been caused by the large amount of carbonic oxide generated by the gun-cotton. The absence of residue from the gun-cotton prevents the fouling of guns, and renders it unnecessary to sponge them after each discharge, for the amount of incombustible mineral matter present in the cotton is very small (from 1 to 2 per cent.), and is entirely scattered by the explosion.

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* Too much stress, however, should not be laid upon this as rendering gun-cotton magazines safer in case of fire than gunpowder magazines. The experiment with gunpowder mentioned at page 454 shows that if all the particles of an explosive be raised at once to nearly the inflaming point, the first particle which inflames will cause the detonation of the remainder. Since the inflaming point of gun-cotton is low, the above condition would be easily fulfilled in a conflagration.

It has already been mentioned that the explosion of gun-cotton does not impart so much heat to the metal of the gun as that of powder, the difference being so great that, after firing 100 rounds with gun-cotton, the gun was not so much heated as after 30 rounds with gunpowder. This important advantage of gun-cotton is probably due to the circumstance that the charge of gun-cotton is only one-third of the charge of powder, that the explosion of the former is so much more rapid, leaving less time for the communication of heat to the metal, and that there are no highly heated solid products left in contact with the gun. Gun-cotton wool may be fired upon the palm of the hand with impunity, or upon a heap of gunpowder without kindling it; although it cannot be doubted that the temperature of the flame is really much higher than the inflaming point of powder. That the recoil of a gun charged with gun-cotton is only two-thirds of that experienced with gunpowder is probably due to the rapidity of the explosion, which allows less time for overcoming the inertia of the gun; the difference in recoil taking the form of strain upon the metal composing the gun.

It is evident, from the consideration of its manufacture, that gun-cotton is entirely uninjured by water, so that a store of this explosive is kept immersed in water; whereas gunpowder is, of course, rendered useless by contact with water, which dissolves out the nitre. Even when exposed to very damp air, gunpowder is liable to injury from the effect of moisture in partially separating the nitre from the other ingredients, whilst gun-cotton only requires exposure to a dry atmosphere for a short time to render it fit for use. The proportion of moisture retained by gun-cotton, in the ordinary state of the atmosphere, is 2 per cent.

As an objection to the employment of gun-cotton as a substitute for gunpowder, it has been asserted that the cellulo-trinitrine is liable to undergo spontaneous decomposition, which might at any time render the contents of a magazine unserviceable, or might even give rise to the evolution of a sufficient amount of heat to cause an explosion. The origin of this objection is to be traced to the old process for preparing gun-cotton, in which the acids were not allowed to act upon the cotton for a sufficient length of time, so that the whole of the cotton was not converted into true gun-cotton, but some less stable substitution-products were formed at the same time. Another cause of spontaneous alteration is the imperfect washing of the gun-cotton, whereby minute traces of acid are left in the fibre. All recent experiments, by Abel and others, appear to have proved that, considering its highly complex character, *pure* gun-cotton is a very stable compound under ordinary conditions; although, when kept in a moist state, it develops traces of acid-products, the temperature does not rise to any important extent, nor is the explosive quality of the material at all injured. A little carbolic acid is sometimes added to wet gun-cotton kept in store, to prevent the growth of mould.

542. *Soluble pyroxylin*, or *collodion-cotton*, $C_{18}H_{21}O_6(HO)(NO_3)_8$, is the product of the action upon cellulose of a mixture of nitric and sulphuric acids slightly diluted with water ($HNO_3 + H_2SO_4 + 1\frac{3}{4}H_2O$). It differs from pyroxylin in being soluble in a mixture of ether with one-seventh of alcohol, yielding a viscous solution, which leaves the transparent collodion film when evaporated. It is much less rapidly combustible than pyroxylin.

In order to prepare the soluble cotton for collodion, 3 measured ounces of ordinary nitric acid (sp. gr. 1.429) are mixed with 2 ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp. gr. 1.839) are added to this mixture, which is continually stirred whilst the acid is being added. A thermometer is placed in the mixture, which is allowed to cool to 140° F.; 100 grains of dry cotton wool, in ten separate tufts, are immersed in the mixture for five minutes, the beaker being covered with a glass plate. The acid is then poured into another beaker, the cotton squeezed with a glass rod, and thrown into a large volume of water; it is finally washed in a stream of water till it is no longer acid, and dried by exposure to air.

Collodion balloons.—These balloons may be made in the following manner:—Six grains of collodion-cotton, prepared according to the above directions, are dissolved in a mixture of 1 drachm of alcohol (sp. gr. .835) and 2 drachms of ether (sp. gr. .725) in a corked test-tube. The solution is poured into a dry Florence flask, which is then turned about slowly, so that every part of its surface may be covered with the collodion, the excess of which is then allowed to drain back into the tube. Air is then blown into the flask through a long glass tube attached to the bellows as long as any smell of ether is perceptible. A penknife blade is carefully inserted between the flask and the neck of the balloon, which is thus detached from the glass all round; a small piece of glass tubing is introduced for an inch or two into the neck of the balloon, so that the latter may cling round it. Through this tube air is drawn out by the mouth, until one-half of the balloon has left the side of the flask and collapsed upon the other half; by carefully twisting the tube, the whole of the balloon may be detached and drawn out through the neck of the flask, when it must be quickly untwisted, distended by blowing through the tube, tied with a piece of silk, and suspended in the air to dry. The average weight of such balloons is 2 grains.

Celluloid, or *artificial ivory*, or *xylonite*, used for combs, billiard balls, &c., is essentially compressed collodion-cotton mixed with camphor and zinc oxide.

When collodion-cotton is kept for some time, especially if at all damp, it undergoes decomposition, filling the bottle with red fumes, and becoming converted into a gummy mass, which contains oxalic acid.

543. By acting upon cellulose with a mixture represented by the formula $HNO_3 + H_2SO_4 + 2H_2O$, the compound $C_{18}H_{21}O_6(HO)_2(NO_3)_7$ is produced, which is soluble in ether and in glacial acetic acid.

When the composition of the mixture corresponds to $HNO_3 + H_2SO_4 + 2\frac{1}{2}H_2O$, a fourth compound, $C_6H_7O_2(HO)(NO_3)_2$, is produced, which does not dissolve in hot glacial acetic acid, and is sparingly soluble in alcohol and ether.

The lowest common denomination of the molecule of cellulose under which these compounds can be brought is $(C_6H_{10}O_5)_3$; the *cellulo-nitrins*, or *nitric ethers of cellulose*, will then be as follow—

$C_{18}H_{21}O_6(NO_3)_9$, insoluble in alcohol and ether and in glacial acetic acid.
$C_{18}H_{21}O_6.HO.(NO_3)_8$, soluble in alcoholic ether; insoluble in acetic acid.
$C_{18}H_{21}O_6(HO)_2(NO_3)_7$, soluble in ether and in acetic acid.
$C_{18}H_{21}O_6(HO)_3(NO_3)_6$, insoluble in acetic acid.

The existence of these compounds indicates for cellulose the formula $C_{18}H_{21}O_6(OH)_9$, a nonohydric alcohol.

544. *Para-cellulose* is distinguished from cellulose by not dissolving in ammonio-cupric solution until it has been boiled with very dilute hydrochloric acid; it is found in the epidermic cells of leaves and in root-tissue.

Meta-cellulose is insoluble in ammonio-cupric solution, even after boiling with hydrochloric acid; it also differs from cellulose by dissolving in cold moderately dilute sulphuric acid. It occurs chiefly in fungi and lichens.

Vasculose, $C_{18}H_{20}O_8$, is the chief constituent of the vessels which bind the wood-cells and fibres together. It may be obtained by boiling the pith of the willow with very dilute HCl to convert the para-cellulose into cellulose, and then digesting it with ammonio-cupric solution to dissolve the cellulose. Vasculose is dissolved when heated, under pressure, to 130° C. with moderately strong alkaline solutions, to a brown liquid which gives a dark brown precipitate with acids. This is turned to account for extracting vasculose from the crude fibre, such as wood and straw, intended for the manufacture of paper, the cellulose being left. It is also acted on by oxidising agents, such as chlorine-water and chloride of lime, which do not attack cellulose, but convert vasculose into resinous substances soluble in alkalies. When distilled, vasculose yields methyl alcohol, which is not obtained from cellulose. It also yields more acetic acid than cellulose.

The proportion of vasculose increases with the hardness and density of the wood. Poplar contains 18 per cent. of vasculose and 64 per cent. of cellulose and para-cellulose, whilst oak contains 28 per cent. of vasculose and 53 of cellulose and para-cellulose, and iron wood (*Ostrya virginica*) contains 40 per cent. of vasculose and 27 of cellulose and para-cellulose. The shells of nuts contain more vasculose in proportion to their hardness; walnut shells contain 44 per cent., and cocoa-nut shells 58 per cent. Vasculose is always accompanied in the wood by resinous matters, which give rise to the difference of colour in woods, and by a small quantity of nitrogenised matter, and of ash deposited with it from the sap.

Cutose is obtained from the outer layer of the epidermis of leaves and fruits by extracting with boiling dilute hydrochloric acid, ammonio-cupric solution, alcohol, and ether (to extract waxy bodies). It is much richer in carbon and hydrogen than cellulose, containing 68.29 per cent. of C, 8.95 per cent. of H, and 22.76 per cent. of oxygen. Cutose dissolves slowly in boiling dilute solutions of alkalies and their carbonates, and is reprecipitated by acids. When dissolved in concentrated solution of potash, there are separated, on adding an acid, two easily fusible acids resembling fatty acids; these are *oleocutic acid*, $C_{14}H_{20}O_4$, and *stearocutic acid*, $C_{28}H_{48}O_4$. Cutose is believed to be a compound of these acids.

Cutose appears to be identical with the suberin found in *cork*, which is found to contain 43 per cent. of cutose, 29 of vasculose, 12 of cellulose and para-cellulose, and 9 per cent. of substances soluble in ether and alcohol.

Tunicin, $C_6H_{10}O_5$, or *animal cellulose*, is prepared from the outer covering or *mantle* of the mollusks belonging to the class *Tunicata*. The mantle is long boiled with hydrochloric acid and potash, in succession, and the residue washed with water, alcohol, and ether. Tunicin is left as a translucent mass, so closely resembling cellulose in properties that it is believed by some chemists to be identical with it.

Chitin, $C_9H_{15}NO$, is the chief constituent of the shells of crabs, lobsters, and beetles, and is left after exhausting them with water, alcohol, ether, acetic acid, and alkalies. It is a white translucent substance, which dissolves in cold concentrated sulphuric acid, giving a solution which yields glucose when diluted.

545. GLUCOSIDES.—The compounds belonging to this class are capable of conversion into a sugar and some other compound by the action of acids, alkalies, and certain ferments, the change being generally the result of *hydrolysis* or decomposition attended by appropriation of the elements of water. They are chiefly found in plants, and generally yield products of decomposition belonging to the aromatic group. Some of them have been already noticed.

Salicin, $C_{13}H_{18}O_7$, is extracted from willow-bark (*Salix*) by boiling it in water, removing the colouring matter and tannin from the solution by boiling with lead hydrate, precipitating the excess of lead by H_2S, and evaporating the filtered liquid, when the salicin crystallises in needles which may be recrystallised from alcohol. It forms bitter colourless prisms which dissolve in about 30 parts of cold water; it is more soluble in alcohol, but insoluble in ether. It is readily distinguished by the bright red colour which it gives with strong sulphuric acid, which detects it when applied to the inner bark of the willow. When fermented by emulsin (p. 504) or saliva, its aqueous solution yields glucose and salicyl-alcohol or *saligenin*—

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH).CH_2.OH.$$

The saligenin gives a blue colour with ferric chloride.

When solution of salicin is boiled for some time with dilute sulphuric or hydrochloric acid, it yields an amorphous precipitate of *saliretin*, a product of the decomposition of saligenin—

$$2C_7H_8O_2\ (\textit{saligenin}) = H_2O + C_{14}H_{14}O_3\ (\textit{saliretin}).$$

Sulphuric acid and potassium dichromate convert salicin into oil of spiræa (p. 505). Fused with potash, it yields potassium salicylate (p. 524). Dilute nitric acid converts salicin into *helicin*—

$$C_{13}H_{18}O_7 + O = C_{13}H_{16}O_7 + H_2O.$$

This is also a glucoside, yielding glucose and oil of spiræa when hydrolysed by ferments or acids; $C_{13}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_7H_6O_2$. Strong nitric acid converts salicin into *nitrosalicylic acid*, $C_6H_3.OH.NO_2.CO_2H$. When acted on by chlorine, salicin yields substitution-products containing one, two, and three atoms of chlorine, and these, when boiled with dilute acids yield the corresponding chlorosaligenins.

Salicin is occasionally administered as a febrifuge, and is a common adulteration of quinine.

Populin, or *benzoyl-salicin*, $C_{13}H_{17}(C_7H_5O)O_7$, is a sweet crystalline body existing, together with salicin, in the bark and leaves of the aspen (*Populus tremula*), a tree of the Willow order, and may be extracted in the same way as salicin. When boiled with barium hydrate, it yields salicin and benzoic acid (which becomes barium benzoate); $C_{13}H_{17}(C_7H_5O)O_7 + H_2O = C_{13}H_{18}O_7 + C_7H_5O.OH$. Boiled with dilute acids, it is converted into benzoic acid, saliretin, and glucose. It is obtained artificially by fusing salicin with benzoic anhydride—

$$C_{13}H_{18}O_7 \ + \ (C_7H_5O)_2O \ = \ C_{13}H_{17}(C_7H_5O)O_7 \ + \ C_7H_5O.OH.$$

Arbutin, $C_{12}H_{16}O_7$, is found in the leaves of the bear-berry (*Arbutus uva ursi*), an astringent plant of the Heath order, sometimes used medicinally, and in *Pyrola umbellata*, also a medicinal plant of the closely allied Winter-green order. It may be prepared like salicin, and crystallises in bitter needles from its aqueous solution. Emulsin or dilute acids decompose it into glucose and hydroquinone; $C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2$.

Phlorizin, $C_{21}H_{24}O_{10}$ (φλοιός, bark, and ῥίζα, *root*), is extracted by hot alcohol from the root-bark of the apple, pear, plum, and cherry tree. It crystallises from hot water in bitter needles with 2Aq. When boiled with dilute acids, it yields glucose and *phloretin*; $C_{21}H_{24}O_{10} + H_2O = C_6H_{12}O_6 + C_{15}H_{14}O_5$. When exposed to air in the presence of ammonia, it is converted into a fine purple colouring matter, *phlorizeïn*, $C_{21}H_{30}N_2O_{13} = (C_{21}H_{24}O_{10} + 2NH_3 + O_3)$.

Glycyphyllin, $C_{21}H_{24}O_9$, is a crystalline substance allied to phlorizin, extracted from the leaves of *Smilax glycyphylla*, an Australian plant of the Sarsaparilla order. It is sparingly soluble in cold water, but dissolves in hot water and in alcohol. Its solution tastes like liquorice. It does not reduce alkaline copper solutions, and is not precipitated by normal lead acetate, though it is by the basic acetate. When boiled with dilute sulphuric acid, it yields phloretin and *isodulcite*—

$$C_{21}H_{24}O_9 \ + \ 2H_2O \ = \ C_{15}H_{14}O_5 \ + \ C_6H_{14}O_6.$$

Hesperidin, $C_{22}H_{26}O_{12}$, is contained in the fruit, leaves, and stalks of the orange-tree and other members of the same family; it is resolved by acids into glucose and *hesperitin*, $C_{16}H_{14}O_6$.

Æsculin, $C_{15}H_{16}O_9$, is extracted by boiling water from the bark of the horse-chestnut (*Æsculus hippocastanum*), sometimes used as a febrifuge. The infusion of the bark is mixed with lead acetate, to precipitate the tannin and colouring matter, filtered, the excess of lead precipitated by H_2S, and the filtered solution evaporated, when æsculin crystallises in colourless needles containing 2Aq, sparingly soluble in cold water, but readily in hot water and in alcohol. The aqueous solution is slightly bitter, and has a strong blue fluorescence, destroyed by acids, and restored by alkalies. Emulsin and boiling dilute acids convert æsculin into glucose and *æsculetin*; $C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4$. Æsculetin exists, in small quantity, in horse-chestnut bark. *Paviin* or *fraxin* accompanies æsculin in horse-chestnut bark. It is more soluble in ether than æsculin, and has a green fluorescence. Fraxin is obtained in larger quantity from the bark of the ash (*Fraxinus excelsior*) which is also febrifugal. Trees of the genus *Pavia*, belonging to the same order as horse-chestnut (*Soapworts*), yield more paviin than æsculin. The formula of paviin is not settled.

546. *Amygdalin*, $C_{20}H_{27}NO_{11}$, is extracted from bitter almonds, the kernels of the fruit of *Amygdalus communis*, of which one variety yields the sweet almond, containing no amygdalin. The almonds are pressed to extract the fixed oil (not the *essential oil*, but a glyceride), and the *bitter almond cake* is boiled with alcohol, from which the amygdalin crystallises in pearly scales which dissolve in water, and crystallise from it in prisms with 3Aq. Amygdalin may also be extracted from the kernels of peaches and nectarines, both fruits of varieties of amyg-

dalus. It is also present in the leaves and kernels of several species of cherry, and the bitter almond oil formed from it confers the flavour upon cherry-brandy, noyau, ratafia, and maraschino. The production of glucose, hydrocyanic acid, and benzoic aldehyd, by the action of emulsin on solution of amygdalin, has been already noticed (p. 504). When long boiled with baryta, it yields ammonia and the barium-salt of *amygdalic acid*, $C_{20}H_{28}O_{13}$. This acid is a glucoside, for when boiled with dilute acids it is converted into glucose and *mandelic acid*; $C_{20}H_{28}O_{13} + 2H_2O = 2C_6H_{12}O_6 + C_8H_8O_3$. Mandelic acid (mandel, *almond*; German) is really *phenyl-glycolic acid*, $CH.C_6H_5.OH.CO_2H$, and may be obtained from bitter-almond oil by combining it with hydrocyanic acid to form $C_6H_5.COH.HCN$, and boiling with hydrochloric acid, which produces mandelic acid and ammonium chloride—

$$C_6H_5.COH.HCN \;+\; HCl \;+\; 2H_2O \;=\; CH.C_6H_5.OH.CO_2H \;+\; NH_4Cl.$$

On evaporating and treating with ether, the mandelic acid is dissolved out. It is metameric with anisic acid.

Daphnin, $C_{15}H_{16}O_9$, isomeric with æsculin, is obtained from the bark of *Daphne mezereum*, used as a remedy for toothache. Dilute acids convert it into glucose and *daphnetin*; $C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4$.

Convolvulin, $C_{31}H_{50}O_{16}$, and its homologue *jalapin*, $C_{34}H_{56}O_{16}$, are the purgative principles of certain of the *Convolvulaceæ*, such as *jalap* and *scammony*. They are amorphous bodies, which yield glucose, and, respectively, *convolvulinol*, $C_{13}H_{24}O_3$, and *jalapinol*, $C_{16}H_{30}O_3$, when hydrolysed by acids or emulsin. *Turpethin*, isomeric with jalapin, is extracted from the roots of *Convolvulus turpethum*, also used as a purgative.

Helleborein, $C_{26}H_{44}O_{15}$, is the narcotic poison from the root of *black hellebore*, a plant of the Buttercup order. It crystallises in needles, which dissolve easily in water, but sparingly in alcohol.

Digitalin, $C_{54}H_{84}O_{27}$, is the poisonous glucoside extracted from the seeds of the foxglove (*Digitalis purpurea*). It is crystalline, sparingly soluble in water and ether, but dissolves in alcohol and chloroform. Strong sulphuric and hydrochloric acids dissolve it with a green colour.

Saponin, $C_{32}H_{54}O_{18}$, is found in the soap-wort, in the root of the clove-pink, which belongs to the same natural order (*Caryophyllaceæ*), in the pimpernel, and in the fruit of the horse-chestnut. It may be extracted by boiling alcohol, which deposits it as an amorphous powder on cooling. It is soluble in water, and its solution lathers like soap. This leads to the use of decoctions containing it, such as that of the soap-nut of India, for cleansing delicate fabrics. The dry powder of saponin causes sneezing.

Coniferin, $C_{16}H_{22}O_8.2Aq$, crystallises from the gummy liquid found in the spring between the inner and outer barks of coniferous trees. In contact with water and emulsin, it yields glucose and *coniferyl alcohol*—

$$C_{16}H_{22}O_8 \;+\; H_2O \;=\; C_6H_{12}O_6 \;+\; C_{10}H_{12}O_3.$$

The latter is a crystalline body, soluble in ether, and smelling of vanilla. When distilled with potassium dichromate and sulphuric acid, it yields acetic aldehyd and *vanillin*; $C_{10}H_{12}O_3 + O = C_2H_4O + C_8H_8O_3$. (*See* Vanillic aldehyd, p. 506.)

Quercitrin, $C_{33}H_{30}O_{17}$, is the colouring matter of quercitron bark, and is also found in horse-chestnut flowers, and in grape-vine, sumach, and catechu. It may be extracted from quercitron bark by alcohol, the tannin precipitated by solution of gelatin, and the filtrate evaporated. Quercitrin forms yellow crystals, sparingly soluble in water. Dilute sulphuric acid converts it into *isodulcite* and *quercetin*; $C_{33}H_{30}O_{17} + H_2O = C_6H_{14}O_6 + C_{27}H_{18}O_{12}$. This last, also called *flavin*, is found in heather, in tea, and in the root bark of apple and other trees. It is a yellow crystalline body, which is sparingly soluble in water and more soluble in alcohol. It may be sublimed in yellow needles. *Rutin*, which occurs in rue and in capers, much resembles quercitrin.

Glycyrrhizin, or *liquorice-sugar*, $C_{24}H_{36}O_9$, is a glucoside extracted from liquorice-root (*Glycyrrhiza glabra*) by boiling water; on adding lead acetate to the solution, a lead compound is precipitated, and if this be filtered off, washed, suspended in water, and decomposed by H_2S, the glycyrrhizin passes into solution and may be obtained as a yellow amorphous residue on evaporation. It has a sweet taste, and yields glucose and *glycyrretin* when boiled with dilute acids—

$$C_{24}H_{36}O_9 + H_2O = C_{18}H_{26}O_4 + C_6H_{12}O_6.$$

Antiarin, $C_{14}H_{20}O_5.2Aq.$, is the principle of the Javanese arrow-poison, *upas-antiar*, the juice of *Antiaris toxicaria*, a large tree of the Bread-fruit tribe. It may be crystallised from the alcoholic extract of upas, and is soluble in water and ether. With acids, it behaves like a glucoside.

547. Unclassified vegetable principles resembling glucosides. — *Picrotoxin*, $C_{12}H_{14}O_5$, is a narcotic poison contained in *Cocculus indicus*, the fruit of *Anamirta paniculata*, a tropical trailing shrub of the order *Menispermaceæ*. The fruit has been sometimes used as a *hop-substitute* by brewers. Picrotoxin may be extracted from the seeds by boiling with alcohol, from which it crystallises in needles; it is sparingly soluble in water, and soluble in ether. *Quassiin*, $C_{10}H_{12}O_3$, is another crystalline bitter principle, extracted by alcohol from *quassia* chips, the wood of *Picrasma excelsa* (bitterwood). This is also said to be used as a hop-substitute, and is not poisonous, except to flies. It is administered as a tonic. Water dissolves it sparingly, but acquires a bitter taste. *Calumbin*, $C_{21}H_{22}O_7$, is a substance of the same kind, extracted from *calumba root* (*Cocculus palmatus*). *Santonin*, $C_{15}H_{18}O_3$, is the bitter principle of the seeds of *Artemisia santonica* (*worm-seed*) and of *Artemisia absinthium* (*wormwood*); it may be extracted from absinthium by mixing it with lime and boiling with weak alcohol; the solution is evaporated and the residue boiled with acetic acid, which deposits colourless prisms of santonin, which become yellow when exposed to light. It is insoluble in water, but dissolves in alcohol and ether; it is dissolved by alkalies, yielding santonates, *e.g.*, *sodium santonate*, $NaC_{15}H_{19}O_4$, from which *santonic acid*, $HC_{15}H_{19}O_4$, may be obtained by shaking with HCl and ether. Santonin is moderately poisonous, and affects the perception of colours; it is contained in the liqueur known as *crême d'absinthe*, or *Wermuth*. *Gentianin*, $C_{14}H_{10}O_5$, is extracted by ether from the roots of the yellow gentian, used as a bitter and tonic. It forms yellow needles, sparingly soluble in water, but freely in alcohol and ether; also soluble in alkalies, with a strong yellow colour. *Elaterin* (ἐλατήριος, driving away, in allusion to its drastic quality), $C_{20}H_{28}O_5$, is the active principle of the drug *elaterium*, obtained from the juice of the squirting cucumber (*Momordica elaterium*). It is crystalline, insoluble in water, but soluble in alcohol and ether. It admits of sublimation.

Kosine, $C_{31}H_{38}O_{10}$, is the active principle of *Kousso*, an Abyssinian plant used as a vermifuge; it crystallises in yellow needles, which are insoluble in water, but soluble in ether and alcohol. *Aloin*, $C_{17}H_{18}O_7$, is a crystalline bitter-sweet substance extracted from *aloes*, the dried juice of various species of aloe.

Coumarin, $C_9H_6O_2$, is the substance which causes the smell of hay and of the Tonka bean (*Coumaroma odorata*), from which it may be extracted by boiling with alcohol, when crystals of coumarin are deposited on cooling. It has been obtained artificially from the oil of meadow-sweet, salicyl hydride, by treating it with sodium, and decomposing the sodium salicylide with acetic anhydride—

$$\underset{\text{Sodium salicylide.}}{NaC_7H_5O_2} + \underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} = \underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Acetyl-salicylide.}}{C_2H_3O.C_7H_5O_2};$$

$$\text{and } C_2H_3O.C_7H_5O_2 = H_2O + \underset{\text{Coumarin.}}{C_9H_6O_2}$$

548. Vegetable colouring matters.—Notwithstanding the great variety and beauty of the tints exhibited by plants, comparatively few yield colouring matters which are sufficiently permanent to be employed in the arts, the greater number of them fading rapidly as soon as the plant dies, since they are unable to resist the decomposing action of light, oxygen, and moisture, unless supported by the vital influence in the plant; some of them even fade during the life of the plant, as may be seen in some roses which are only fully coloured in those parts which have been screened from the light. The vegetable colouring matters may be classed under three divisions: (1) those which exist ready formed in the plant, such as turmeric and safflower; (2) those which are formed by the conjoint action of alkalies

and oxygen, as in the cases of logwood and archil; (3) those which belong to the class of glucosides.

Chlorophyll (from χλωρός, *green*; φύλλον, *a leaf*), the abundant green colour of plants, has not been obtained in a perfectly pure state, on account of its inability to crystallise or volatilise. The want of exact knowledge of the chemistry of this body is especially felt because its physiological importance to plants is of the highest order. It is evidently active in constructing the tissues of the plant from carbonic acid, water, ammonia, &c., derived from the air and soil. It may be extracted from the leaves of plants by boiling with alcohol, or ether, or benzene. The purest product yet obtained was prepared by allowing the alcoholic extract of the leaves to stand for some time, filtering off the deposit, and shaking the filtrate with one volume of ether and two volumes of water. The ethereal layer, which contains all the chlorophyll, is shaken with water as long as the latter reduces alkaline copper solution; it is then allowed to evaporate, when it leaves the chlorophyll as a bright green residue. When this is dissolved in alcohol, and boiled with dilute sulphuric or hydrochloric acid, the solution gives the glucose reaction with alkaline copper solution, rendering it probable that chlorophyll is a glucoside.

Chlorophyll dissolves, in cold strong sulphuric acid, to a green solution which gives a dark green precipitate on dilution, and the filtrate gives the glucose reaction. If the green precipitate or the original chlorophyll is boiled with alcoholic potash, the solution, when neutralised with hydrochloric acid, gives a yellow precipitate (*phylloxanthin*), and the solution retains a blue colouring matter (*phyllocyanin*) which contains nitrogen. The autumnal colour of leaves is perhaps due to the disappearance of the phyllocyanin. Green leaves assume an autumnal tint when immersed in chlorine. Iron is said to be an essential constituent of chlorophyll.

The blue colouring matter contained in many flowers, such as the violet, has been named *cyanin*. Acids redden it, and hence only those flowers which have a neutral juice are blue; red flowers yielding an acid juice. The colouring matter of grapes and of red wine appears to be cyanin.

549. *Saffron* is a yellow colouring matter, obtained from the flowers of *Crocus sativus*, which are purple with yellow anthers. When these are dried and pressed into cakes they form the saffron of commerce, which has an agreeable odour. It is chiefly imported from Spain, and is often adulterated with marigold petals. It gives up to water and alcohol a yellow amorphous substance, termed *polychroite*, $C_{48}H_{60}O_{18}$, a glucoside, which, when boiled with dilute sulphuric acid, yields glucose, *crocin*, $C_{16}H_{18}O_6$, and a volatile oil, $C_{10}H_{16}O$, smelling of saffron. *Annatto*, or arnotto, is another yellow colouring matter, which forms the pulp round the seeds of *Bixa orellana*, a West Indian shrub. It is used for colouring butter and cheese. The colouring principle has been called *bixin*; it is sparingly soluble in water, but dissolves in alcohol and in alkalies; acids reprecipitate it without much change of colour.

Turmeric is the root of an East Indian plant, the *Curcuma longa*, and is used in curry. It contains a crystalline yellow body, *curcumin*, $C_{10}H_{10}O_3$, which may be extracted by boiling with benzene. It is insoluble in water, but dissolves in alcohol, with a green fluorescence. Alkalies dissolve it, forming red salts, from which acids precipitate it of a yellow colour. Paper dyed with turmeric is used as a delicate test for alkalies, which turn it brown. When acted on by boric acid and strong sulphuric acid, it is converted into *rosocyanin*, which crystallises in green needles dissolved by alcohol, with a red colour, which is changed to deep blue by alkalies. Turmeric-paper is used in testing for boric acid.

Weld is the *Reseda luteola*, a plant of the Mignonette order, the leaves of which give a yellow solution when boiled with water. The hot decoction, mixed with alum and chalk, gives a yellow precipitate, which is used in paper-staining. It contains a crystalline yellow body, *luteolin*, $C_{20}H_{14}O_8$, sparingly soluble in water, but dissolved by alcohol and by alkalies. It sublimes in yellow needles.

Fustic is a yellow dye stuff, of which there are two kinds. *Old fustic* is the wood of a tree of the Mulberry order (*Morus*, or *Maclura tinctoria*), grown in the West Indies. *Young fustic* is the wood of *Rhus cotinus*, or Venice sumach, from Italy and the South of France. When old fustic is boiled with water, the solution deposits yellow needles of *morin*, $C_{12}H_{10}O_6$, soluble in alcohol. The mother-liquor of morin, when evaporated, yields *maclurin*, a nearly colourless body. When fused with potash, morin yields phloroglucin, and maclurin yields, in addition, *protocatechuic acid*. Maclurin is identical with moritannic acid; it gives a dark green precipitate with ferric chloride.

Gamboge is a yellow gum-resin, originally obtained from Camboja in Asia, and is exuded by certain species of Guttiferæ. It contains about 30 per cent. of a yellow gum, soluble in water, and 70 per cent. of resin soluble in alcohol and alkalies, called *gambodic acid*.

Purrée, or *Indian yellow*, imported from India and China, is a compound of magnesia with *euxanthin* (or *euxanthic acid*), $C_{19}H_{16}O_{10}$. By extracting it with hydrochloric acid and alcohol, the euxanthin is obtained in yellow prisms, sparingly soluble in water, soluble in alcohol, ether, and alkalies. When heated, it yields a yellow crystalline sublimate of *euxanthone*, $C_{13}H_8O_4$. On fusion with potash, euxanthone yields hydroquinone, and nitric acid converts it into trinitroresorcin, which oppose the idea that purrée is of animal origin.

550. *Safflower*, which yields *rouge*, consists of the dried flowers of *Carthamus tinctorius*, cultivated in Egypt. It contains a yellow substance, which may be extracted by water, and a red colour, *carthamin*, $C_{14}H_{16}O_7$, which may be dissolved out by sodium carbonate, and precipitated by acetic acid. Alcohol dissolves it to a red solution. It is used in dyeing, but soon fades when exposed to light.

Carotin, $C_{18}H_{24}O$, is a red substance, found in small crystals in the cells of the carrot. It crystallises from alcohol in cubes of agreeable odour.

Santalin, $C_{15}H_4O_5$, is the colouring matter of *red sanders wood* (*Pterocarpus santalinus*), from which it may be extracted by alcohol, which deposits it in red crystals insoluble in water, but giving violet solutions with alkalies.

Hæmatoxylin, $C_{16}H_{14}O_6.3H_2O$, is extracted from *logwood* (*Hæmatoxylon campechianum*), which grows at Campeachy in the Bay of Honduras, by boiling the chips with water. It is deposited from the solution in yellow needles, which are soluble in water, alcohol, and ether. It resembles the phenols by dissolving in alkalies to a purple solution, which absorbs oxygen and forms a red colouring matter, *hæmatein*, $C_{16}H_{12}O_6$, sparingly soluble in cold water, which may also be obtained by oxidising hæmatoxylin, in ethereal solution, with nitric acid. Reducing agents, such as sulphurous acid, convert it into hæmatoxylin. When fused with potash, hæmatoxylin yields pyrogallol.

Potassium chromate gives an intense black colour with infusion of logwood, which has been used as an ink, but is fugitive. Logwood boiled with distilled water gives a yellow solution, but with common water it gives a fine purple red, from the production of hæmatein by the oxidation of the hæmatoxylin in presence of the calcium carbonate in the water. The solution of logwood is sometimes used as an *indicator* in alkalimetry.

Brazilin, $C_{22}H_{18}O_7$, is contained in Brazil wood (*Cæsalpiniea brasiliensis*), peachwood (*C. echinata*), and Sappan wood (*C. sappan*)—all dyewoods from the same botanical sub-order as logwood. Brazilin, when quite pure, forms colourless crystals, and yields colourless solutions in air-free water and alcohol; but it soon becomes yellow by oxidation, and dissolves in alkalies with a fine red colour, which is bleached by reducing agents.

The colouring matters from *madder* and *litmus* have been already noticed.

551. *Indigotin*, or *indigo blue*, $C_{16}H_{10}N_2O_2$, is prepared from *Indigofera tinctoria* and *cærulea*, plants belonging to the same natural order (*Leguminosæ*) as those furnishing the dye-woods mentioned above, and, like the colours obtained from those, it does not exist as such in the plant, but as a product of alteration of a nearly colourless body termed *indican*.

Indican, $C_{52}H_{62}N_2O_{34}$, is extracted from the leaves and twigs of the plant by digestion with cold alcohol, which leaves it, when evaporated, as a brownish syrupy liquid of bitter taste. Indican is a glucoside, and is hydrolysed by fermentation or by boiling with dilute acids, yielding *indiglucin* and *indigotin*—

$$C_{52}H_{62}N_2O_{34} + 4H_2O = 6C_6H_{10}O_6 + C_{16}H_{10}N_2O_2.$$

Indiglucin has not been crystallised; it is a sweetish syrupy liquid which reduces alkaline copper solution, but does not ferment. The indigotin is obtained as a blue precipitate. For the preparation of indigo on the large scale, the plants are cut just before they blossom, chopped up, covered with cold water, and allowed to ferment for twelve or fifteen hours, when the indican is decomposed, and the indigotin, under the reducing influence of the fermentation, is converted into *hydrindigotin*, or *indigo-white*, $C_{16}H_{12}N_2O_2$. As soon as a blue scum appears upon the surface, a little lime is added, and the yellow liquid is run into shallow vats and well beaten with sticks to promote the action of air, which oxidises the indigo-white to indigo-blue; $C_{16}H_{12}N_2O_2 + O = C_{16}H_{10}N_2O_2 + H_2O$. The indigo-blue is precipitated and collected, on calico strainers, to be pressed and cut up into cakes. As purchased, indigo-blue contains about half its weight of indigotin; it may be purified by boiling, first, with acetic acid, which extracts a substance termed *indigo gluten*, then with weak potash, to extract *indigo-brown*, and, lastly, for some time with alcohol, which removes *indigo-red*.

Indigotin may also be prepared from commercial indigo by boiling it with aniline, which deposits the indigotin in crystals on cooling.

When commercial indigo is carefully heated, it is converted into a violet vapour, which condenses in dark blue needles, with a coppery reflection.

Indigotin is insoluble in water, alcohol, ether, and diluted acids and alkalies. Strong sulphuric acid and, more easily, fuming sulphuric acid, dissolve it, forming *indigotin-monosulphonic acid*, $C_{16}H_9(SO_2.OH)N_2O_2$, and *indigotin-disulphonic* or *sulphindylic acid*, $C_{16}H_8(SO_2.OH)_2N_2O_2$. On adding water, a blue precipitate of the mono-acid is obtained, which is soluble in pure water and in alcohol. It is monobasic, and its concentrated solution gives a purple precipitate of the potassium-salt on addition of potassium acetate. The precipitate produced by potassium carbonate in the solution of indigo in sulphuric acid is known as *indigo carmine*, and consists chiefly of *potassium sulphindylate*—

$$C_{16}H_8(SO_2.OK)_2N_2O_2;$$

it is soluble in water. The sulphonic acids of indigo are bleached by zinc-dust, being converted into the corresponding acids of indigo white, which become blue again when shaken with air. Sulphindylic or *sulphindigotic* acid is used in dyeing *Saxony blue* cloth.

Indigo white is prepared by shaking powdered indigo with 2 parts of ferrous sulphate, 3 parts of slaked lime, and 200 parts of water, in a stoppered bottle placed in warm water, till the indigo has dissolved to a yellow liquid, when the calcium sulphate and ferroso-ferric hydrate are allowed to subside, and the clear solution drawn off into dilute hydrochloric acid in a vessel from which air has been expelled by CO_2. The hydrindigotin is precipitated in white flakes, which quickly become blue indigo when exposed to air. Other reducing agents are sometimes substituted for ferrous sulphate in preparing the *indigo-vat*. A mixture of indigo, madder, potassium carbonate, and lime, left to ferment, gives an alkaline solution of *reduced indigo*. Sodium hydrosulphite (p. 212) and lime are also employed for this purpose. When linen and cotton are immersed in the indigo-vat and exposed to air, the indigo white is oxidised to indigo blue, which is precipitated upon the fabric. Hydrindigotin precipitated by acids from its alkaline solutions becomes crystalline after a time; it is soluble in alcohol and ether.

When indigo is heated with dilute nitric acid, it is oxidised into isatin, which gives a yellow solution, and sulphindylic acid is sometimes employed as a test for nitric acid. By fusion with potash, it is converted, first into *potassium anthranilate*, $C_6H_4(NH_2)CO_2K$, and afterwards into anilin, $C_6H_5.NH_2$, which distils over. This indicates a near relationship of indigo to the benzene or aromatic group.

552. *Artificial indigo.*—Cinnamic acid, which belongs to the aromatic group, when treated with nitric acid, is converted into *nitrocinnamic acid*, $C_6H_4.NO_2.C_2H_2.CO_2H$. This combines directly, with two atoms of bromine, to form *dibromo-nitro-phenyl-propionic acid*—

$$C_2H_2Br_2.C_6H_4.NO_2.CO_2.H.$$

When this is treated with caustic soda, two molecules of HBr are removed, producing the sodium salt of *nitrophenylpropiolic acid*, $C_2.C_6H_4.NO_2.CO_2H$. By heating this with a reducing agent, such as an alkaline solution of glucose, the latter is made to appropriate the oxygen of two molecules of water, the hydrogen of which acts upon the acid, converting it into indigotin—

$$2(C_8H_4.NO_2.CO_2H) + 2H_2 = C_{16}H_{10}N_2O_2 + 2H_2O + 2CO_2.$$

Cinnamic acid itself may be prepared from the toluene of coal-naphtha (p. 477), $C_6H_5.CH_3$, by acting upon it with chlorine to obtain *benzylene dichloride*, $C_6H_5.CHCl_2$, which is then converted into *benzaldehyd*, $C_6H_5.CHO$, by treatment with potash. The benzaldehyd, when acted on by acetyl chloride, is converted into cinnamic acid—

$$C_6H_5.CHO + CH_3COCl = C_6H_5.C_2H_2.CO_2H + HCl.$$

The production of indigo from coal by this process is at present too expensive to be commercially successful.

553. *Isatin*, $C_8H_5NO_2$, is prepared by oxidising indigo with nitric or chromic acid. It crystallises in orange-coloured prisms, soluble in boiling water and alcohol. When heated, it sublimes with partial decomposition. It dissolves in potash to a violet solution, and is precipitated again by acids. Silver nitrate added to the potash solution gives a carmine-red crystalline precipitate of *silver isatin*, $C_8H_4AgNO_2$. Isatin forms crystalline compounds with alkaline bisulphites (like the aldehyds and ketones). It yields anilin when distilled with strong potash; nitric acid converts it into nitrosalicylic and picric acids. With chlorine it yields *chlorisatin*, $C_8H_4ClNO_2$, and *dichlorisatin*, $C_8H_3Cl_2NO_2$, which are also formed when chlorine acts upon indigo. When these are distilled with potash, they yield mono- and di-chloranilin. Reducing agents convert isatin into *hydro-isatin*, or *isatyde*, $C_8H_6NO_2$.

Indol, C_8H_7N, is formed when indigo is distilled with zinc-dust, or when nitro-cinnamic acid, $C_8H_6NO_2.CO_2H$, is reduced by zinc and potassium hydrate. It crystallises in colourless fusible prisms of disagreeable odour. It boils at about 245° C., and is partly decomposed, but it may be distilled in a vacuum or with steam. It is soluble in water and has weak basic properties, forming a sparingly soluble hydrochloride. A shaving of deal moistened with hydrochloric acid and exposed to its vapour assumes a deep red colour. The hydrochloric solution is coloured red by potassium nitrite. Indol is produced by the action of the peculiar ferment of the pancreatic juice upon the albumen of blood or eggs, and the indican occasionally present in the urine appears to be formed from it.

Skatol, C_9H_9N, homologous with indol, is also a product of the pancreatic fermentation of albumen. It is the chief constituent of the volatile portion of human excrements, whence its name (*σκατός, of dung*). It may be crystallised from hot water in colourless plates, which fuse at 94°, and have a fæcal odour. Skatol is found among the products of the distillation of strychnine with lime.

Trioxindol, or *isatic acid*, $C_8H_7NO_3$, is obtained as a potassium salt when a potash solution of isatin is boiled till it becomes yellow; HCl then separates isatic acid as a white powder, which yields isatin and water when heated. *Dioxindol*, $C_8H_7NO_2$, is a crystalline body formed by reducing isatin with zinc-dust and HCl, or by acting upon sodium isatate with sodium-amalgam. It becomes red in air from production of isatin. When heated, it yields anilin, from which it differs only by 2CO. Gently heated with nitric acid, it yields bitter-almond oil, $C_6H_5.COH$, *Oxindol*, C_8H_7NO, is obtained by reducing di-oxindol with tin and hydrochloric acid. It is colourless, crystalline, soluble in water, alcohol, and ether, and, with care, may be sublimed unchanged.

554. *Lac* is a red dye extracted from the resinous exudation of certain tropical trees of the Fig tribe, punctured by an insect (*Coccus*). In its crude, natural state, encrusting the small branches, it is known as *stick-lac*, and has a deep red colour; when broken off the branches and boiled with water containing sodium carbonate, it gives a red solution, from which the colouring matter is precipitated as a *lake* by adding alum, and made into cubical cakes for the market. The resinous matter (about 68 per cent.) left undissolved by sodium carbonate, is termed *seed-lac;* this is melted, strained through a cloth, and allowed to solidify in thin layers, when it forms *shell-lac*, which is much used in the manufacture of sealing-wax and varnishes. The *lacquer* applied to brass is named after this resin, being an alcoholic solution of shell-lac, sandarach, and Venice turpentine. *Indian ink* is made by mixing lamp-black with a solution of 100 grains of lac in 20 grains of borax and 4 ounces of water.

Carmine owes its colour to *carminic acid*, $H_2C_{17}H_{16}O_{10}$, a glucoside extracted by boiling water from the cochineal insect, which is found upon a species of cactus in Mexico and Peru. *Carmine lake* is the aluminium carminate precipitated by alum and potassium carbonate from the aqueous extract of the cochineal insect. The acid itself is an amorphous purple solid, easily soluble in water and alcohol, and sparingly in ether. It dissolves unchanged in strong sulphuric acid, and the solution is used in thermometers, as a coloured liquid not evolving vapour. The solution of cochineal is very sensitive to alkalies, which change it to purple, and it is used in measuring the alkalinity of waters. Boiled with dilute sulphuric acid, it yields *carmine-red*, $C_{11}H_{12}O_7$, and a non-fermentable sugar.

555. ARTIFICIAL ORGANIC BASES.—A series of homologous bases is obtained from coal-tar, the members of which are isomeric with those furnished by the distillation of some of the alkaloids with potash.

From alkaloids.		*From coal-tar.*
Quinoline	C_9H_7N	Leucoline
Lepidine	$C_{10}H_9N$	Iridoline
Dispoline	$C_{11}H_{11}N$	Cryptidine

Quinoline, or *chinoline*, is prepared by the action of sulphuric acid (50 parts) and nitrobenzene (12 parts) upon aniline (19 parts) and glycerin (60 parts). The mixture is cautiously heated to 130° C. in a flask with a reflux-condenser, the lamp being removed when the reaction begins; it is then again heated for three hours, and distilled with lime, when quinoline distils over together with aniline, from which it may be separated by fractional distillation. The nitrobenzene acts as an oxidising, and the sulphuric acid as a dehydrating, agent—

$$C_3H_5(OH)_3\ (\textit{glycerin}) + C_6H_5NH_2\ (\textit{aniline}) + O = C_9H_7N\ (\textit{quinoline}) + 4H_2O.$$

Quinoline is also obtained by distilling quinine, cinchonine, or strychnine with potash, and in the destructive distillation of coal and bones. It is a colourless liquid of tarry smell, of sp. gr. 1.08 and boiling point 238° C. It is sparingly soluble in water, and is a tertiary amine. It combines with amyl iodide to form a compound which, when heated with potash, yields a fine blue colour soluble in alcohol, and termed *quinoline-cyanine*—

$$2(C_9H_7N.C_5H_{11}I) + KHO = H_2O + KI + C_{28}H_{35}N_2I$$

Lepidine yields a similar compound, and both are used in silk dyeing. The cyanines crystallise in plates which have a green lustre; they are di-acid bases, and their salts are colourless. *Leucoline*, isomeric with quinoline, boils at 220° C. and does not form a cyanine.

When quinoline is treated with sulphuric acid, it yields a sulphonic acid, from which *hydroxyquinoline*, $C_9H_6(OH)N$, may be obtained. Nascent hydrogen converts this into $C_9H_{10}(OH)N$, and, by treating this with methyl iodide, the hydroxyl hydrogen is exchanged for methyl, and the body, $C_9H_{10}(OCH_3)N$, or $C_{10}H_{13}NO$, is produced. This substance resembles quinine ($C_{20}H_{24}N_2O_2$), and its hydrochlorate is used medicinally, under the name of *kairin*, as a substitute for quinine.

556. *Bases distilled from bones.*—The destructive distillation of bones yields ammonia and other bases, produced by the decomposition of the *bone-gelatine*, or *osséin*, which forms about 30 per cent. of the bones, and contains about 18 per cent. of nitrogen. These bases form an homologous series known as the *pyridine* bases, and many of them are also found in coal tar. They are liquids of disagreeable odour, and belong to the class of tertiary monamines (p. 574). They may be extracted from the offensive oil known as *Dippel's animal oil*, obtained by distilling bones, by shaking the oil with warm dilute sulphuric acid, which dissolves the bases as sulphates, and yields them up on adding potash or soda. They are separated from each other by fractional distillation. Their boiling points are given in the Table.

Pyridine	C_5H_5N	117° C.	Parvoline	$C_9H_{13}N$	188° C.
Picoline	C_6H_7N	133	Coridine	$C_{10}H_{15}N$	211
Lutidine	C_7H_9N	154	Rubidine	$C_{11}H_{17}N$	230
Collidine	$C_8H_{11}N$	179	Viridine	$C_{12}H_{19}N$	251

Pyridine bases are often present in commercial ammonia, and cause it to become pink when neutralised with hydrochloric acid.

Pyridine is obtained by heating amyl nitrate with P_2O_5, which removes the elements of water; $C_5H_{11}NO_3 = 3H_2O + C_5H_5N$. It is also formed when a mixture of hydrocyanic acid and acetylene is passed through a red-hot tube; $HCN + 2C_2H_2 = C_5H_5N$. Pyridine is soluble in water, and forms a deliquescent hydrochloride. When heated with sodium for some time, pyridine is converted into *dipyridine*, $C_{10}H_{10}N_2$, a solid, fusing at 108° C., and subliming in needles. In contact with hydrochloric acid and tin, pyridine is hydrogenised and becomes piperidine, $C_5H_{11}N$ (p. 603), which is reconverted into pyridine by heating to 300° C. with sulphuric acid; $C_5H_{11}N + 3H_2SO_4 = C_5H_5N + 3SO_2 + 6H_2O$.

Picoline, C_6H_7N, is isomeric with aniline, but it boils at 135° (instead of 184°), and is a tertiary amine, whereas aniline, $NH_2.C_6H_5$, is a primary amine. It is obtained by distilling acrolein-ammonia; $C_6H_6O.NH_3 = H_2O + C_6H_7N$. Also by heating glyceryl tribromide, in a sealed tube, to 250° C. with alcoholic solution of ammonia; $2C_3H_5Br_3 + NH_3 = 6HBr + C_6H_7N$. Picoline is very similar in properties to pyridine.

Collidine, $C_8H_{11}N$, results from the reaction between ethylidene chloride and ammonia at 160° C.; $4C_2H_4Cl_2 + NH_3 = C_8H_{11}N + 8HCl$. It is also a product of the decomposition by heat of aldehyd-ammonia. Collidine differs from pyridine and picoline by being sparingly soluble in water.

Pyrrol, C_4H_5N, is a weak liquid base occurring in coal-tar and in Dippel's oil, from which it may be extracted by sulphuric acid, and distilled over from the sulphates of the stronger bases. It is a liquid of ethereal odour, boiling at 133° C., and becoming brown when exposed to air. Heated with dilute acids, it yields a precipitate of *pyrrol-red*; $3C_4H_5N + H_2O = C_{12}H_{11}N_2O + NH_3$. Vapour of pyrrol imparts a red colour to pine wood dipped in hydrochloric acid. Pyrrol is found among the products of the distillation of ammonium pyromucate—

$$NH_4.C_5H_3O_3 = C_4H_5N + CO_2 + H_2O.$$

557. CRYSTALLINE ANIMAL PRODUCTS NOT HITHERTO DESCRIBED.—*Glycocholic acid*, $C_{26}H_{43}NO_6$, exists in *bile* as a sodium salt, together with the sodium salt of *taurocholic acid*, $C_{26}H_{45}NSO_7$. To extract them, *ox-gall* is mixed with bone-black to a paste, which is dried on the steam-bath and digested with absolute alcohol, which dissolves the sodium salts

together with cholesterin and cholin. The solution is mixed with ether, which precipitates the sodium salts. These are dissolved in water, and decomposed by dilute sulphuric acid, which precipitates the glycocholic acid, at first amorphous, but changing into colourless needles. It is sparingly soluble in water, but dissolves in alcohol, though not in ether. Glycocholic acid is monobasic; the potassium and sodium salts are very soluble and sweet. It is characterised by its behaviour with solution of sugar and strong sulphuric acid, which give a purple-red colour (*Pettenkofer's test for bile*). It is an amido-acid, and yields *chologlycolic acid*, $C_{26}H_{42}NO_7$, when treated with nitrous acid. When boiled with alkalies, glycocholic acid is hydrolysed into glycocine (amido-acetic acid) and *cholic acid*; $C_{26}H_{43}NO_6 + H_2O = C_2H_3.NH_2.O_2 + C_{24}H_{40}O_5$. Boiling with dilute hydrochloric acid effects the same change, but converts the cholic acid into *dyslysin*, $C_{24}H_{36}O_3$, which forms an amorphous precipitate; boiling with alcoholic potash converts it into potassium cholate. Taurocholic acid is not precipitated by normal lead acetate, which precipitates the glycocholic acid from ox-gall, and the filtrate gives a precipitate of lead taurocholate on adding basic lead acetate. When this is suspended in water and decomposed by H_2S, a solution of the acid is obtained, which may be concentrated and mixed with ether, when the acid separates as a syrup which deposits needle-like crystals. Dog's bile yields more taurocholic acid than that of the ox. Taurocholic acid dissolves readily in water and alcohol. It is decomposed, like glycocholic acid, by boiling with alkalies or acids, but it yields *taurine*, $C_2H_7NSO_3$, instead of glycocine; $C_{26}H_{45}NSO_7 + H_2O = C_2H_7NSO_3 + C_{24}H_{40}O_5$.

558. *Taurine*, or *amido-ethyl-sulphonic acid*, $C_2H_4.NH_2.SO_3H$, is prepared by boiling ox-gall with dilute HCl, evaporating to dryness on the steam-bath, and treating the residue with absolute alcohol, which leaves the taurine undissolved. This is dissolved in water, from which it crystallises in large four-sided prisms sparingly soluble in cold water, and insoluble in alcohol and ether. It fuses at 240° C. and is decomposed. It has no acid reaction, but it forms salts with bases. When fused with potash, it yields the acetate and sulphite of potassium—

$$C_2H_4.NH_2.SO_3H + 3KOH = C_2H_3KO_2 + K_2SO_3 + NH_3 + H_2O + H_2.$$

Nitrous acid replaces its NH_2 by HO and converts it into isethionic acid; $C_2H_4.NH_2.SO_3H + HNO_2 = C_2H_4.HO.SO_3H + H_2O + N_2$. This has led to the *synthesis of taurine*; ethene (olefiant gas) is absorbed by SO_3, the product dissolved in water, neutralised with ammonia, and evaporated to crystallisation—

$$C_2H_4 + SO_3 + H_2O + NH_3 = C_2H_4.HO.SO_3NH_4 \text{ (\textit{ammonium isethionate})}.$$

When this is heated to 220° C., it yields taurine; $C_2H_4.HO.SO_3.NH_4 = C_2H_4.NH_2.SO_3H + H_2O$. Taurine may also be synthesised by converting ethene into glycol chlorhydrin, $HO.C_2H_4.Cl$, heating this with potassium sulphite, to obtain *potassium isethionate*—

$$HO.C_2H_4.Cl + K_2SO_3 = HO.C_2H_4.SO_3K + KCl;$$

distilling the isethionate with phosphoric chloride—

$$HO.C_2H_4.SO_3K + PCl_5 = PO_2Cl + HCl + KCl + Cl.C_2H_4.SO_2Cl \text{ (\textit{isethionic chloride})};$$

heating this with water—

$$Cl.C_2H_4.SO_2Cl + HOH = HCl + Cl.C_2H_4.SO_2.OH \text{ (\textit{chlor-ethylsulphonic acid})};$$

and heating this to 100° C. with ammonia in a sealed tube—

$$Cl.C_2H_4.SO_2.OH + 2NH_3 = NH_3HCl + NH_2.C_2H_4.SO_2.OH \text{ (\textit{taurine})}.$$

It is probable that some taurine exists as such in the bile; it has been found in the kidneys, lungs, and muscles.

When solution of taurine is evaporated with potassium cyanate, it yields *potassium tauro-carbamate*, $C_2H_4.NHCO.NH_2.SO_3K$; tauro-carbamic acid is found in the urine when taurine is taken internally; it forms crystals easily soluble in water.

Choline, which is also obtained from bile, may be obtained synthetically from ethene by converting it into glycol-chlorhydrin, and heating this with trimethylamine in aqueous solution—

$$HO.C_2H_4.Cl + N(CH_3)_3 + H_2O = HO.C_2H_4.N(CH_3)_3OH + HCl.$$

It is a strongly alkaline ammonium base, which crystallises with difficulty. Choline may also be prepared from yolk of egg and from the brain.

Neurine, which is also prepared from the brain, has the formula $HO.C_2H_3.N(CH_3)_3$, differing from choline by H_2O. It may be obtained from choline by heating it with hydriodic acid, which yields $I.C_2H_4.N(CH_3)_3.I$, and this, decomposed by silver hydrate, gives $HO.C_2H_3.N(CH_3)_3$, or *trimethyl-vinyl-ammonium hydroxide;* it has a strongly alkaline reaction, but has not been crystallised.

Cholesterin, $C_{26}H_{43}.OH$, is a crystalline alcohol found in bile, and composing the chief part of *gall-stones* or biliary calculi, from which it may be extracted by boiling with alcohol, which deposits the cholesterin in transparent lustrous plates on cooling. It is insoluble in water, but soluble in ether; fuses at 145° C. and sublimes at 200° C. It is unchanged by boiling with potash, and yields ethereal salts when heated with the fatty acids in sealed tubes. HCl converts it into *cholesteryl chloride*, $C_{26}H_{43}.Cl$, and ammonia into *cholesteramine*, $C_{26}H_{43}.NH_2$. When dissolved in petroleum and treated with sodium, it evolves hydrogen and forms crystalline $C_{26}H_{43}.ONa$. When moistened with strong nitric acid and dried, cholesterin gives a yellow residue which becomes red with ammonia. Strong HCl and a little ferric chloride give a violet-blue colour with cholesterin on evaporation. Cholesterin occurs in the blood, in brain, in yolk of egg, and in some vegetables, as pease and wheat. It is also found in sheep's wool, together with *isocholesterin*, having the same composition, but crystallising in needles, which fuse at 137° C.

559. *Glycocine*, or *glycocoll*, or *amido-acetic acid*, $C_2H_3.NH_2.O_2$, or $NH_2.CH_2.CO_2H$, is prepared by heating hippuric acid (benzoyl amido-acetic) for half an hour with 4 parts of strong HCl, which converts it into benzoic acid and glycocine hydrochloride—

$$\underset{\textit{Hippuric acid.}}{N.C_7H_5O.H.CH_2.CO_2H} + HCl + H_2O = \underset{\textit{Benzoic acid.}}{C_7H_5O.OH} + \underset{\textit{Glycocine hydrochloride.}}{NH_2.CH_2.CO_2H.HCl}$$

The solution is mixed with water and cooled, when most of the benzoic acid crystallises out; the filtrate is evaporated to dryness on a steam-bath, the glycocine hydrochloride extracted by water, boiled with lead hydrate, filtered from the lead oxychloride, the dissolved lead precipitated by H_2S, and the filtrate evaporated, when it deposits the glycocine in transparent rhombic prisms, easily soluble in water, sparingly in alcohol, and insoluble in ether. Glycocine has a sweet taste, fuses at 170° C., and evolves ammonia and methylamine when further heated. Its solution gives a red colour with ferric chloride, and a blue with cupric sulphate; if this blue solution be mixed with potash and alcohol, it deposits blue needles of the formula $(NH_2.CH_2.CO_2)_2Cu.Aq.$ A sparingly soluble silver salt, $NH_2.CH_2.CO_2.Ag$, may also be obtained, but these compounds do not behave like ordinary salts of the metals. Like other amido-acids, glycocine plays the part of a base and an acid. It forms hydrochlorides containing, respectively, one and two molecules of glycocine, and the latter forms a crystalline platinum salt. Crystalline compounds of glycocine with salts are also known.

When glycocine is heated with barium hydrate, it yields methylamine and barium carbonate—

$$NH_2.CH_2.CO_2H + Ba(OH)_2 = NH_2.CH_3 + BaCO_3 + H_2O.$$

Nitrous acid converts glycocine into glycolic acid—

$$NH_2.CH_2.CO_2H + HNO_2 = N_2 + H_2O + HO.CH_2.CO_2H,$$

for glycocine is metameric with glycolamide, $HO.CH_2.CO.NH_2$ (p. 588).

Synthesis of glycocine.—Bromacetic acid, $CH_2Br.CO_2H$, heated with ammonia, yields glycocine, $CH_2.NH_2.CO_2H$, and ammonium bromide. Glycocine is also formed when cyanogen is passed into a boiling saturated aqueous solution of hydriodic acid—

$$2CN + 2H_2O + 5HI = CH_2.NH_2.CO_2H + NH_4I + 2I_2.$$

Glycocine was formerly called *sugar of gelatin*, since it may be obtained by boiling gelatin with dilute sulphuric acid or with potash.

Sarcosine, or *methyl-glycocine*, $CH.CH_3,NH_2.CO_2H$, or $C_3H_7NO_2$, may be obtained by heating bromacetic acid with methylamine (in place of ammonia, which yields glycocine). It is also formed when the kreatine extracted from flesh is boiled with baryta. Caffeine yields it under similar treatment. Sarcosine forms prismatic crystals, very soluble in water and of sweet taste. It is sparingly soluble in alcohol, insoluble in ether, and may be sublimed. Its reaction is neutral, but it combines with acids and bases.

Betaine, or *tri-methyl-glycocine*, $C(CH_3)_2.NH_2.CO_2(CH_3)$, is found in the juice of beet-root (*Beta vulgaris*), and may be formed synthetically by the action of trimethylamine on chloracetic acid—

$$CH_2Cl.CO_2H + N(CH_3)_3 = C(CH_3)_2.NH_2.CO_2(CH_3) + HCl.$$

Betaine hydrochloride is also obtained by the careful oxidation of choline hydrochloride—

$$C_2H_4.OH.N(CH_3)_3Cl + O_2 = C_2H_2.O.OH.N(CH_3)_3Cl + H_2O.$$

Betaine is soluble in water and alcohol, and forms salts with the acids.

560. *Creatine*, or *kreatine* (*κρέας, flesh*), $C_4H_9N_3O_2$, is obtained from chopped flesh by soaking it in cold water, squeezing it in a cloth, heating the liquid till the albumen coagulates, straining, adding baryta to precipitate phosphoric acid, and evaporating the filtrate to a syrup on the steam-bath; on standing for some hours, the kreatine crystallises out. It may also be prepared from Liebig's extract of meat by dissolving it in 20 parts of water, adding tribasic lead acetate, filtering, removing the excess of lead by H_2S, and evaporating to crystallisation. Granular crystals of kreatine are sometimes met with in Liebig's extract. The flesh of fowls yields 0.32 per cent. of kreatine, that of cod-fish 0.17, beef 0.07 per cent.

Kreatine forms prismatic crystals easily soluble in hot water, but very sparingly in alcohol and ether. The crystals are $C_4H_9N_3O_2.Aq$. Kreatine is neutral in reaction, but plays the part of a weak monacid base. *Kreatine nitrate*, $C_4H_9N_3O_2.HNO_3$, crystallises in prisms. When the solutions of its salts are heated above 30° C., they are converted into salts of kreatinine, a stronger base containing H_2 and O less than kreatine. When boiled with baryta-water, kreatine yields sarcosine and urea (which is afterwards hydrolysed into NH_3 and CO_2), the latter indicating the presence of the cyanamide group, $NC.NH_2$, which would be converted into urea, $CO(NH_2)_2$, by addition of H_2O—

$$C_3H_7NO_2.NC.NH_2\ (\textit{kreatine}) + H_2O = C_3H_7NO_2\ (\textit{sarcosine}) + CO(NH_2)_2.$$

Kreatine has been prepared synthetically by heating cyanamide with an alcoholic solution of sarcosine. When kreatine is warmed with solution of sodium hypobromite, two atoms of its nitrogen are liberated, the third, which is probably existing as CN, being retained. By heating kreatine in aqueous solution with mercuric oxide, it is converted into oxalic acid and *methyl-guanidine*, $N.CH_3.H.CNH.NH_2$. Guanidine itself, $NH_2.CNH.NH_2$ (page 621), is a product of the action of ammonia on cyanamide—

$$C_4H_9N_3O_2\ (\textit{kreatine}) + O_2 = (CO_2H)_2\ (\textit{oxalic acid}) + C_2H_7N_3\ (\textit{methyl guanidine}).$$

This formation of oxatyle would indicate the existence of the CN group, and kreatine might be represented as

$$(CH_2.CN)(NCH_3H)NH_2.CO.OH.$$

Creatinine, or *kreatinine*, or *methyl-glycolyl-guanidine*, $C_4H_7N_3O$, is prepared by heating kreatine in a water-bath and passing a current of pure HCl over it as long as any water is formed. The hydrochloride thus obtained is dissolved in water, decomposed by lead hydrate, the solution filtered and slowly evaporated, when it deposits prismatic crystals of $C_4H_7N_3O.2Aq$, which lose water on exposure to air, becoming opaque. If it be dissolved in cold water, and evaporated *in vacuo*, the original hydrated crystals are reproduced, but if it be dissolved in boiling water and the solution evaporated, it deposits tabular crystals which contain no water. The solution of these crystals when kept for some time at 60° C. deposits the prismatic hydrated kreatinine.

Kreatinine is much more soluble in water than kreatine, requiring about 12 parts of cold water. It dissolves in about 100 parts of cold alcohol. It has an alkaline reaction, and is a strong monacid base. It is characterised by forming a sparingly soluble crystalline compound with zinc chloride, $(C_4H_7N_3O)_2ZnCl_2$. In contact with water, especially in presence of bases, kreatinine is converted into kreatine by hydration. When kreatinine is boiled with baryta-water, it yields ammonia and *methyl-hydantoin*: $C_4H_7N_3O + H_2O = NH_3 + C_4H_6N_2O_2$. This compound is the methylated derivative of *hydantoin*, or *glycolyl-urea*, $CO.N_2H_2.CH_2.CO$, and it is eventually decomposed into sarcosine, CO_2 and NH_3—

$$C_4H_6N_2O_2 + 2H_2O = C_3H_7NO_2 + CO_2 + NH_3.$$

Kreatinine does not appear to exist as such in flesh, though it is easily produced from it by the dehydration of the kreatine. A substance having the same composition as kreatinine exists in considerable quantity in urine (about two grammes in the urine of twenty-four hours), but its properties are not quite the same as those of the kreatinine prepared from the kreatine of flesh. In order to prepare urinary kreatinine, the urine is mixed with one-twentieth of its volume of a cold saturated solution of sodium acetate, and with one-fourth of its volume of a cold saturated solution of mercuric chloride; this produces an amorphous precipitate which is quickly filtered off, and the filtrate is set aside for forty-eight hours, when it deposits a granular precipitate, appearing in spheres under the microscope. The composition of this precipitate when dried over sulphuric acid is $4(C_4H_7N_3O.HCl.HgO).3HgCl_2$. This precipitate is suspended in cold water, and decomposed by H_2S, the mercuric sulphide is filtered off, and the acid filtrate evaporated over sulphuric acid, when it leaves crystals of the hydrochloride, $C_4H_7N_3O.HCl$. The concentrated aqueous solution of this salt is decomposed, in the cold, with lead hydrate, when an alkaline filtrate is obtained, which has a bitter taste, and, by spontaneous evaporation, yields prismatic crystals of

$C_4H_7N_3O.2H_2O$, which rapidly become opaque and anhydrous when exposed to air. If heat be employed during the preparation of the body, tabular crystals of $C_4H_7N_3O$ are obtained, which are unchanged by exposure to air.

The urinary kreatinine requires 362 parts of cold alcohol to dissolve it, while flesh-kreatinine requires only 102 parts. The platinum-salt of the former is $2(C_4H_7N_3O.HCl).PtCl_4.2H_2O$, whereas that of the flesh-kreatinine is anhydrous. Urinary kreatinine is a more powerful reducing agent than that prepared from flesh-kreatine; on adding mercuric chloride and excess of potash, it gives a precipitate which is yellowish-white at first, but rapidly becomes black from reduction of mercury. Both kreatinines reduce alkaline copper solution, but 4 molecular weights of the urinary kreatinine are equal in reducing power to 5 of the flesh-kreatinine. When the urinary kreatinine is boiled with much water for some time, it is converted into kreatine, but if this be converted into kreatinine hydrochloride by heating in HCl gas, the salt crystallises from a cold aqueous solution in efflorescent crystals, while the hydrochloride of urinary kreatinine is always anhydrous. Moreover, the gold-salt of the natural kreatinine, $C_4H_7N_3O.HCl.AuCl_3$, is unchanged by ether, which decomposes the gold-salt of the artificial base, dissolving the auric chloride and leaving kreatinine hydrochloride (G. S. Johnson, *Proc. Roy. Soc.*, xlii. 365; *Chem. News*, lv. 304).

561. *Leucine*, or *amido-caproic acid*, $C_5H_{10}.NH_2.CO_2H$, is prepared by boiling horn shavings (one part) with sulphuric acid ($2\frac{1}{2}$ parts) and water ($6\frac{1}{2}$ parts) in a reflux apparatus, for twenty-four hours. The hot liquid is neutralised by lime, filtered, and evaporated to about one-third; it is then carefully neutralised with sulphuric acid and evaporated till crystals of leucine (and tyrosine) are deposited on cooling; it is recrystallised from water, when the tyrosine crystallises first.

Several other animal substances yield leucine and tyrosine when boiled with dilute sulphuric acid, or fused with potash. The *elastine* composing the cervical ligament of the ox yields more than horn. Leucine also occurs extensively in animals and vegetables. It is found in the liver, spleen, lungs, and pancreas; also in caterpillars and spiders; in the white sprouts of vetch, in yeast, and in putrefying cheese.

Leucine crystallises in pearly scales, moderately soluble in water, slightly in alcohol, and insoluble in ether. It fuses at 170°, and may be partly sublimed, though much of it decomposes, yielding amylamine; $C_5H_{10}.NH_2.CO_2H = NH_2.C_5H_{11} + CO_2$. Its reaction is neutral, but it forms compounds both with acids and bases. Hydriodic acid converts it into caproic acid and ammonia—

$$C_5H_{10}.NH_2.CO_2H + 2HI = C_5H_{11}.CO_2H + NH_3 + I_2.$$

With nitrous acid it yields *leucic* or *hydroxy-caproic* acid—

$$C_5H_{10}.NH_2.CO_2H + HNO_2 = C_5H_{10}.OH.CO_2H + N_2 + H_2O.$$

Leucine is obtained synthetically from ammonia and bromocaproic acid; $NH_3 + C_5H_{10}Br.CO_2H = C_5H_{10}.NH_2.CO_2H + HBr$; also by the reaction between valeraldehyd-ammonia, hydrocyanic acid, hydrochloric acid, and water—

$$C_5H_{10}O.NH_3 + HCN + HCl + H_2O = C_5H_{10}.NH_2.CO_2H + NH_3.HCl.$$

Tyrosine, or *oxy-phenyl-amido-propionic acid*—

$$C_6H_4(OH).C_2H_3.NH_2.CO_2H,$$

is obtained, together with leucine, when albuminoid or gelatinoid bodies are boiled with dilute sulphuric acid or fused with potash. It crystallises in needles which are sparingly soluble, even in hot water, sparingly soluble in alcohol, and insoluble in ether. Like leucine, it behaves both as a weak acid and a weak base. When its aqueous solution is boiled with mercuric nitrate it gives a yellow precipitate which becomes red when boiled with nitric acid containing nitrous acid. Acted on by chlorine, tyrosine yields chloranil, $C_6Cl_4O_2$, and when fused with potash it yields ammonia and the (para)hydroxy-benzoate and acetate of potassium—

$$C_6H_4.OH.C_2H_3.NH_2.CO_2H + 2KHO = NH_3 + C_6H_4.OH.CO_2K + CH_3.CO_2K + H_2.$$

Guanine, $C_5H_5N_5O$, is extracted from guano (the excrement of sea-fowl) by boiling it with lime and water, and boiling the undissolved residue with soda, which dissolves the guanine and uric acid; these are precipitated by acetic acid, and the guanine dissolved out by hydrochloric acid, and precipitated by ammonia. It is amorphous, insoluble in water and alcohol, and acts as a weak di-acid base and a weak dibasic acid. It is very nearly related to uric acid ($C_5H_4N_4O_3$); when evaporated with nitric acid, it leaves a yellow residue which becomes purple red with soda. Oxidised by potassium chlorate and hydrochloric acid, it yields CO_2, parabanic acid, and guanidine—

$$C_5H_5N_5O + O_3 + H_2O = CO_2 + C_3H_2N_2O_3 + C.NH.(NH_2)_2.$$

Guanine is found in the pancreas of the horse, in gouty deposits in pigs, in the excrement of spiders and the scales of bleak. It is formed, together with xanthine and sarcine, when yeast is allowed to decompose in water at 35° C.

Xanthine, $C_5H_4N_4O_2$, is prepared by the action of nitrous acid on guanine; $C_5H_5N_5O + HNO_2 = C_5H_4N_4O_2 + H_2O + N_2$. It forms minute white crystals sparingly soluble in water, insoluble in alcohol, dissolved by alkalies, and reprecipitated by acids. Evaporated with nitric acid it leaves a yellow residue, becoming violet when heated with potash. It yields crystalline salts with acids, but they are decomposed by water. Its ammoniacal solution yields, with silver nitrate, a gelatinous precipitate containing $C_5H_2Ag_2N_4O_2.H_2O$, which, when treated with methyl iodide, yields a compound isomeric with theobromine—

$$C_5H_2Ag_2N_4O_2 + 2CH_3I = C_5H_2(CH_3)_2N_4O_2 + 2AgI.$$

Xanthine occurs in certain rare urinary calculi, and, in small quantity, in urine, in the liver, pancreas, spleen, and brain; also in guano and yeast.

Sarcine, or *hypoxanthine*, $C_5H_4N_4O$, exists in extract of meat, amounting to about 0.6 per cent., and may be precipitated from the mother-liquor of the extraction of kreatine (p. 674) by boiling with cupric acetate. The brown precipitate is dissolved in nitric acid and precipitated by silver nitrate, which forms an insoluble compound from which the sarcine may be extracted by decomposing with H_2S and boiling with much water. It crystallises in minute needles, and is more soluble than xanthine, though it forms a less soluble hydrochloride. It is feebly basic and acid. Nitric acid oxidises it to xanthine. Sarcine is generally found together with xanthine, and occurs in many parts of the animal body, especially in marrow.

Xanthine and sarcine are both produced when uric acid is acted on by water and sodium amalgam. This reaction, considered together with the conversion of guanine into xanthine by nitrous acid, indicates a simple relationship between these compounds.

Uric acid . .	$C_5H_2(OH)_2N_4O$	Sarcine . .	$C_5H_2(H)_2N_4O$
Xanthine . .	$C_5H_3.OH.N_4O$	Guanine . .	$C_5H_3.NH_2.N_4O$

Carnine, $C_7H_8N_4O_3$, is also found in extract of meat, and much resembles xanthine and sarcine. Nitric acid or bromine-water oxidises it to sarcine. It may possibly be derived from uric acid by substitution of $(CH_3)_2$ for H_2.

Tetanine, $C_5H_{11}N$, has been obtained from the putrefying beef extract used for cultivating a microbe which is alleged to be the cause of tetanus in animals. It is a volatile liquid, boiling at about 100° C., and produces symptoms of tetanus when injected under the skin.

Ptomaines.—Several bases obtained from decomposing animal matter are classed under this name (πτῶμα, *a corpse*). *Neuridine*, $C_5H_{14}N_3$, and *neurine*, $C_5H_{13}NO$, have been obtained from putrid flesh; *muscarine*, $C_5H_{15}NO_3$, and *gadinine*, $C_6H_{17}NO_2$, from putrid fish. *Cadaverine*, $C_5H_{16}N_2$, and *putrescine*, $C_4H_{12}N_2$, have been obtained from a decomposed corpse. *Mydine*, $C_8H_{11}NO$, and *mydatoxine*, $C_6H_{13}NO_2$, have also been obtained.

562. Gelatinoid compounds.—These substances are so called from *gelu*, *ice*, because their solution in hot water becomes a transparent jelly on cooling. *Gelatin* contains 50 per cent. carbon, 25.1 oxygen, 18.3 nitrogen, and 6.6 hydrogen, numbers which approximate to $C_{42}H_{66}N_{13}O_{16}$, but its molecular formula has not been determined, because it cannot be converted into vapour, and does not form well-

defined compounds with other bodies. It may be obtained by digesting bones in cold dilute hydrochloric acid, till the calcium phosphate and other salts are dissolved, leaving a residue of the same form as the bone, but of a soft, flexible character. This is termed osséin, and has the same composition as gelatin, into which it is converted by long boiling with water, especially under pressure, a solution being obtained which becomes a jelly on cooling, and leaves a brittle, transparent mass (*glue*) when dried. Gelatin does not fuse when heated, but swells up and decomposes, yielding very offensive alkaline vapours, containing ammonia and compound ammonias (methylamine, &c.), pyrrol, and its derivatives, toluene, naphthalene, ammonium cyanide, water, &c. *Dippel's oil*, obtained by distilling bones, contains these products, together with others, in the formation of which the fat of the bones takes part, such as the cyanides of the fatty-acid series (propio-nitrile, &c.), pyridine bases, phenol, and aniline.

Gelatin softens and swells in cold water, but does not dissolve; hot water dissolves it, and the solution gelatinises on cooling, even when it contains only 1 per cent. Continued boiling of the solution destroys the tendency to gelatinise. Gelatin is insoluble in alcohol, which precipitates it in white flakes from its aqueous solution. It is also precipitated by tannin, which combines with it to form an insoluble non-putrescible compound. Mercuric chloride also precipitates solution of gelatin. If gelatin solution be mixed with potassium dichromate, the jelly formed on cooling becomes insoluble on exposure to light, which is turned to account in photography; the action probably consists in an oxidation of the gelatin. Acetic acid dissolves gelatin (*liquid glue*); alkalies also dissolve it. When boiled with strong alkalies or with diluted sulphuric acid for a long time, it yields leucine and glycocine (sugar of gelatin). Heated with sulphuric acid and potassium dichromate or manganese di-oxide, gelatin yields numerous products of oxidation, among which are found many of the fatty acids, with their corresponding aldehyds and cyanides, with benzoic acid, bitter-almond oil, &c.

Gelatin may also be obtained by the action of water at a high temperature on skin, sinews, and connective tissue. *Isinglass* is a very pure variety of gelatin prepared from the air-bladder of fish, especially of the sturgeon. *Glue* is made from the refuse and parings of hides, after being cleansed from hair and blood by steeping in lime-water, and exposed to the air for some days to convert the lime into carbonate, and prevent the injurious effect of its alkaline character upon the gelatin. They are then boiled with water till the solution gelatinises firmly on cooling, when it is run off into another vessel, which is kept warm to allow the impurities to settle down, after which it is allowed to set in shallow wooden coolers. The jelly is cut up into slices and dried upon nets hung up in a free current of air. Spring and autumn are usually selected for drying glue, since the summer temperature would liquefy it, and frost would, of course, split it and render it unfit for the market. *Size* is made in a similar manner, but finer skins are employed, and the drying is omitted, the size being used in the gelatinous state. The best size is made from parchment cuttings. Moist gelatin easily putrefies, becoming very offensive; for this reason size is often treated with sulphurous acid.

Chondrin (*χόνδρος*, cartilage) is prepared by the action of water at a high temperature on the cartilages of the ribs and joints, and resembles gelatin in composition and properties. It contains, however, less nitrogen and a small quantity of sulphur. Its composition is 50 per cent. carbon, 28.6 oxygen, 14.4 nitrogen, 6.6 hydrogen, and 0.4 sulphur.

The aqueous solution of chondrin is precipitated by acetic acid, by alum, and by lead acetate, which do not precipitate gelatin. When boiled with dilute sulphuric acid, it yields leucine, but no glycocine. Boiled with hydrochloric acid, it gives a solution which reduces alkaline copper solution like glucose.

Sericin, or *silk-gelatin*, $C_{15}H_{25}N_5O_8$, is the so-called *gum* extracted from silk by boiling with water; it resembles gelatin, but is precipitated by basic lead acetate, and, when boiled with sulphuric acid, yields leucine, tyrosine, and *amidoglyceric acid* (*serin*), $C_2H_4.NH_2.O.CO_2H$. (*Cystine*, $C_3H_7NO_2S$, found in some rare urinary calculi, appears to be a sulphur derivative of serin.)

563. Albuminoid compounds.—Under this head are classed several products of animal and vegetable life, which are not crystalline or volatile, and differ from the gelatinoid bodies by their insolubility in hot water. They resemble each other very closely in composition, containing from 50 to 55 per cent. carbon, 21 to 27 oxygen, 13 to 18.5 nitrogen, 6.7 to 7.3 hydrogen, and 0.4 to 1.7 sulphur. If the sulphur be regarded as essential to the formula, the mean of these numbers would give, approximately, the formula $C_{136}H_{219}N_{35}O_{47}S$, whilst the atomic ratio between the four other elements is nearly $C_{40}H_{62}N_{10}O_{13}$, giving a much higher proportion of nitrogen to carbon than is usual in organic substances.

Albumen, or *white of egg*, $C_{72}H_{108}N_{18}O_{22}S$, may be extracted from its aqueous solution contained in the egg, by stirring it briskly to break up the membrane, adding a little acetic acid to neutralise the soda present in the white, filtering, placing for twelve hours on a dialyser (p. 114) to separate the sodium chloride and acetate, evaporating the contents of the dialyser, below 50° C., powdering the residue, and treating with ether to extract fatty matters. The albumen so prepared is an amorphous solid, of sp. gr. 1.31. When heated, it swells up, carbonises, and evolves offensive alkaline vapours, usually leaving a slightly alkaline ash, containing a trace of calcium phosphate, which is very difficult to separate completely from the albuminoids.

In cold water, albumen slowly softens and dissolves, like gum; if this be heated to about 70° C. (158° F.), the albumen is converted into an insoluble form, becoming a white, soft solid, as in boiled eggs, if the albumen amounts to 12 per cent., and a flocculent precipitate if the solution be diluted. The *coagulated* albumen is not easily dissolved by acids or alkalies, and is believed to be the anhydride of soluble albumen, for if it be heated with water in a sealed tube to above 150° C. (302° F.), it is dissolved to a reddish liquid, which behaves like a solution of ordinary albumen, but is not coagulated by heat. Raw white of egg is inodorous, and does not blacken silver; but after boiling it smells of H_2S, and blackens silver, showing that it suffers some decomposition during coagulation. When dried, the coagulated albumen forms a translucent brittle mass, which becomes white and opaque in water. The soluble form of albumen, completely dried below 50° C., may afterwards be heated to 100° C., without becoming insoluble.

Alcohol precipitates albumen from its solution, and the soluble is converted into the insoluble form by digestion with strong alcohol. It is also precipitated by shaking with ether or turpentine.

In many reactions albumen resembles the amido-compounds, as in playing the part of a weak acid and a weak base. Strong potash added to a solution of albumen precipitates a gelatinous compound of potash and albumen, which is soluble in boiling water, and gives, with metallic salts, precipitates containing albumen and metallic oxides. Acids coagulate the solution of potash-albumen.

The mineral acids, except ortho- and pyro-phosphoric acids, precipitate a solution of albumen, the precipitate being a compound of the acid with albumen, but the organic acids, except picric, do not, as a rule, precipitate it. Many of the compounds of albumen and acids have been proved to have a definite composition. Nitric acid has long been employed as a test for albumen (in urine, for example), since it forms a precipitate even in a very weak solution, but if the liquid be mixed with a very minute quantity of the acid, the flocculent precipitate formed at first disappears on shaking, and the clear acid liquid is not precipitated by boiling. The same thing is observed with sulphuric and hydrochloric acids. Very weak nitric acid, in the course of a few weeks, converts albumen into a yellow mass, which may be washed with cold water, and afterwards dissolves in hot water, and gelatinises on cooling. When nitric acid is added to the solution of potash-albumen, it produces a precipitate, which dissolves in the slightest excess of the acid, reappears on adding more acid, dissolves on boiling, and gelatinises on cooling.

To obtain definite compounds of albumen with the acids, beaten white of egg is placed in a hoop-dialyser floated upon the surface of the very diluted acid for about 24 hours, when the acid passes through the dialyser and combines with the albumen. To prepare the nitrate, an acid containing 1 grm. HNO_3 in 100 c.c. was employed. It formed a semi-transparent jelly which dissolved in boiling water, yielding an acid solution which gelatinised on cooling. On neutralising with an alkali and heating, the albumen was precipitated. Excess of alkali added to the cold solution prevented the coagulation, but did not redissolve the coagulum when added to the hot solution. Dried *in vacuo*, the nitrate was a brittle transparent mass, which swelled up in water, and gradually dissolved. It was not changed at 100° C. The nitric acid in two specimens prepared with acids of different strengths amounted, respectively, to 6.70 and 6.69 per cent. The hydrochloride forms a very transparent, nearly colourless jelly, soluble in hot water; the solution gives no precipitate with silver nitrate until the albumen has been precipitated by nitric acid. Solution of the hydrochloride is precipitated by mercuric chloride and basic lead acetate, which do not precipitate the nitrate. It contains 3.93 per cent. of hydrochloric acid. The sulphate did not gelatinise until a day or two after its removal from the dialyser; the moist jelly carbonised at 100° C., but after drying *in vacuo*, it was unchanged at 100°. The sulphate is not precipitated by mercuric chloride. It contains 5.36 per cent. of H_2SO_4. The orthophosphate does not gelatinise until it is heated, and is not precipitated by mercuric chloride; it contains 8.47 per cent. of H_3PO_4.

The albumen metaphosphate does not gelatinise spontaneously, and when heated it forms an opaque insoluble coagulum; but if heated with an equal bulk of water, it yields, on cooling, a transparent jelly. It contains 4.37 per cent. HPO_3. The citrate resembles the metaphosphate, and contains 6.54 per cent. of $H_3C_6H_5O_7$. Albumen oxalate forms a clear soluble jelly, when heated, or mixed with alcohol, and, when dried, contains 5.32 per cent. of $H_2C_2O_4$. The tartrate resembles the oxalate, and contains 15.63 per cent. of $H_2C_4H_4O_6$. The acetate resembles the metaphosphate and citrate, and contains 5.5 per cent. of $HC_2H_3O_2$. In most cases, the percentages of the acids in the above compounds bear very simple molecular ratios to each other.

The reagents commonly employed for precipitating albumen are nitric acid, mercuric chloride, potassium ferrocyanide, and picric acid. Of these, nitric and picric acids precipitate all the above compounds of albumen with the acids; potassium ferrocyanide precipitates all except the metaphosphate, citrate, and oxalate; mercuric chloride only precipitates the hydrochloride and the metaphosphate.* Two molecules of albumen are completely precipitated by one molecule of potassium ferrocyanide, the precipitate being albumen combined with H_4FeCy_6.

Strong hydrochloric acid gives with albumen a precipitate which dissolves in excess, and gives a purplish solution when boiled in contact with air. Strong nitric acid colours coagulated albumen yellow; alkalies dissolve the yellow mass to an orange liquid, from which acids precipitate yellow flakes (*xantho-proteic acid*).

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* See a Paper by G. Stillingfleet Johnson, "Chem. Soc. Journ." xxvii. 734.

Albumen also gives a fine red colour with mercuric nitrate containing nitrous acid (*Millon's test;* prepared by dissolving mercury in twice its weight of nitric acid, in the cold, and adding twice its bulk of water). By careful treatment with pure nitric acid, albumen is converted into *tri-nitro-albumen*, $C_{72}H_{105}(NO_2)_3N_{18}SO_{22}$, a yellow insoluble body. Strong sulphuric acid dissolves albumen, in the cold, to a brownish liquid, which carbonises when heated, ammonium sulphate being produced. A particle of sugar added to the solution in cold sulphuric acid gives a violet colour. The compound formed by the action of strong sulphuric acid on albumen has been obtained as a white powder of the composition

$$C_{72}H_{107}(SO_3H)N_{18}SO_{22},$$

and is called *albumino-sulphonic acid;* it is insoluble in dilute acids, but soluble in alkalies. A mixture of strong sulphuric and nitric acids converts albumen into *hexanitro-albumino-sulphonic* acid, $C_{72}H_{101}(NO_2)_6(SO_3H)N_{18}SO_{22}$, a bitter yellow powder, insoluble in water, alcohol, and dilute acids, soluble in alkalies to a red solution. Ammonium sulphide converts this into the corresponding amido-compound, $C_{72}H_{101}(NH_2)_6(SO_3H)N_{18}SO_{22}$, which has weak acid properties. When boiled with moderately dilute sulphuric acid, albumen yields leucine and tyrosine (p. 676). With solution of potash, on boiling, it also gives leucine and tyrosine, evolves one-third of its nitrogen as ammonia, and its sulphur is converted into potassium sulphide, which gives a black precipitate on adding a salt of lead. When heated with baryta-water to 150° C., it evolves part of its nitrogen as ammonia, and barium carbonate is formed in the same ratio to the ammonia as when urea is heated with baryta; this has led to the conclusion that albumen contains one-fifth of its nitrogen in a form nearly allied to urea, and that it is probably a complex ureide (p. 592). With manganese dioxide or potassium dichromate, and sulphuric acid, albumen yields products similar to those furnished by gelatin (p. 678). When oxidised by potassium permanganate, it yields benzoic acid. Boiled with a mixture of potassium permanganate and potash, it evolves the whole of its nitrogen as ammonia, whilst with potash alone it only gives off one-third of its nitrogen.

When albumen is heated with bromine and water in a sealed tube, it yields bromoform, leucine, aspartic acid, bromacetic acid, oxalic acid, and a little bromanil, CO_2 being evolved.

564. The gastric juice dissolves coagulated albumen digested with it at about 37° C., and the solution is not precipitated by potassium ferrocyanide nor coagulated by heating. In this condition it is said to have been *peptonised*, or converted into *peptone* (*πέπτω, to digest*). The constituent of the gastric juice which effects this change is termed *pepsin*, and may be precipitated from the juice by alcohol. It resembles albumen in composition, but is much less putrescible. When dissolved in dilute hydrochloric acid it yields a mixture which peptonises most albuminoids if digested at about 40° C. The pepsin prepared from the stomach of the pig and other animals is sometimes administered medicinally to assist digestion.

Serum albumen forms nearly 8 per cent. of the serum of blood, and is found in other liquid secretions. It may be prepared by precipitating the diluted serum with lead acetate, suspending the washed precipitate in water, and decomposing it with CO_2; the filtered liquid is then evaporated below 50° C. It appears to contain less sulphur than ovalbumen in the ratio of 1.2 : 1.6, but rather more oxygen (23.1 : 22.4). In properties it very closely resembles ovalbumen, but it is not coagulated by ether, and gives precipitates with nitric and hydrochloric acids which are more easily dissolved by excess than those of egg albumen. It is more powerfully lævorotatory than egg albumen.

Vegetable albumen is the substance which is precipitated by heat from the juices of plants, and from their infusions in cold water. It has not been obtained pure in the soluble condition. It appears to contain less sulphur even than serum albumen.

Globulin, or *paraglobin*, is very similar in character and composition to albumen, but it is insoluble in pure water; it dissolves in a very weak solution of salt, and in very weak acids and alkalies. It dissolves in water saturated with oxygen, and is precipitated by carbon dioxide. This gas precipitates it in a granular form from the serum of blood; saturation of the serum with salt also precipitates it. Globulin is found in the aqueous humour and crystalline lens of the eye.

Myosin (μῦς, a muscle) is an albuminoid contained in flesh, which is liquid during life and coagulates after death. It may be extracted from chopped flesh by triturating it to a pulp with common salt, adding 9 parts of water for one of salt, digesting for some time at 24° C., pressing through linen and filtering; the myosin is precipitated on adding much water, or by saturating it with salt. The coagulation of the myosin in the muscles is believed to be the cause of the rigidity of the limbs after death.

565. *Fibrin* composes the muscular fibre of flesh, and is contained, to the amount of about 0.4 per cent., in the serum of blood. It differs from the other albuminoids in its tendency to spontaneous coagulation, in which it resembles myosin, but it is not dissolved by solution of salt. It may be obtained from freshly drawn blood by whipping it with a bunch of twigs, when the fibrin adheres to them in threads which become nearly white when washed, and may be freed from fat by alcohol and ether. If the blood be not stirred when freshly drawn, it forms a red *clot* caused by the coagulation of the fibrin, and the entanglement in it of the red blood-globules; if the clot be cut up and washed in a cloth, the globules may be washed away and the fibrin left. If seven measures of blood be drawn into a vessel containing one measure of a cold saturated solution of sodium sulphate, the fibrin will remain in solution, whilst the blood-globules will be deposited on standing. The clear yellow solution containing albumen and fibrin is largely diluted with water, when the fibrin is precipitated.

Fibrin forms elastic strings which dry into a yellow horny mass. When fresh, it readily absorbs oxygen, and evolves CO_2. It is insoluble in water, alcohol, solution of salt, and in cold very dilute HCl (0.1 per cent.), but this dissolves it at 60° C. Solution of nitre at 40° C. also dissolves it. When heated for some time with water at 72° C., it becomes insoluble in dilute acids and salts, but dissolves in alkalies. Boiled for many hours with water, one-fifth of it may be dissolved, yielding a solution having some of the properties of gelatin. Heated with water to 120° C. for some hours, it is almost entirely dissolved. The solution of fibrin in weak HCl is precipitated by neutralisation and by saline solutions. The precipitate always contains a little calcium phosphate. Fibrin soaked in weak potash becomes gelatinous, and if heated to 60° C., dissolves to a solution resembling that of albumen. Fibrin is hardened and rendered non-putrescible when soaked in solution of tannin. Fresh moist fibrin rapidly decomposes hydric peroxide, evolving oxygen. Moist fibrin soon begins to putrefy when exposed to air, and becomes fluid in a week; the products of putrefaction resemble those from albumen. Sulphuric acid and potassium dichromate act upon fibrin as upon albumen, but larger quantities of butyric acid and butyral are obtained.

It appears, from recent investigations, that fibrin does not exist as such in the serum of blood, but that it is produced by the reaction between two varieties of globulin, which takes place as soon as their solution is out of contact with living tissue; one of these (*fibrinoplasmin*) is precipitated by CO_2 from blood deprived of its globules (see above), and the other (*fibrinogen*) is deposited on mixing the concentrated filtrate with alcohol. These may be dissolved in very weak alkali, and the solutions coagulate when mixed.

Fibrin from blood contains more nitrogen than the albumen of serum (17.4 : 15.6) and a little less oxygen (21.8 : 23.1). It does not appear that blood-fibrin and flesh-fibrin are identical.

566. *Casein* is the chief constituent of the curd of milk, and differs from the other albuminoids in not coagulating spontaneously or on heating. It exists in milk as a soluble compound with a little potash or soda, and is separated as curd when the alkali is neutralised either by adding an acid or by the formation of acid (lactic) by the decomposition of milk-sugar caused by spontaneous fermentation. It is prepared by precipitating diluted milk with acetic acid and washing the precipitate with water, alcohol, and ether in succession, to remove soluble matters and fat; it is further purified by dissolving in weak soda and precipitating it by acetic acid. Coagulated casein is characterised by the facility with which it is dissolved by weak alkaline solutions, yielding a liquid upon the surface of which, when boiled, an insoluble pellicle forms, like that produced on the surface of boiled milk. Coagulated casein may also be dissolved by acetic or oxalic acid, but sulphuric or hydrochloric acid reprecipitates it, these acids forming compounds with casein which are insoluble in the acids, but soluble in water. If skimmed milk be carefully evaporated to dryness, and the fat extracted from the residue by ether, the casein is left in the soluble form mixed with milk-sugar, and may be dissolved in water or in dilute alcohol.

Casein combines with slaked lime to form a hard insoluble mass, so that a mixture of cheese with lime is sometimes used as a cement for earthenware. The curd of milk, washed and dried, is used by calico-printers, under the name of *lactarine*, for fixing colours. If it be dissolved in weak ammonia, mixed with one of the aniline dyes, printed on calico, and steamed, the colour is left as an insoluble compound with the casein.

A distinctive property of casein is its coagulation by *rennet*, the mucous membrane of the stomach of the calf, a small quantity of which, or of its infusion in water, coagulates the casein in a large quantity of milk; the coagulation does not appear to depend upon the formation of lactic acid, but upon a specific action of the rennet; the curd thus produced contains calcium and magnesium phosphates, and is not easily soluble in sodium carbonate. The casein of milk is more readily coagulated by acids and by rennet when the milk is warmed; hence milk which has undergone very slight fermentation is curdled when heated, but if fresh milk be heated to boiling, the decomposition will be prevented. The casein of milk is precipitated by some neutral salts, such as sodium chloride or magnesium sulphate, and even by an excess of sodium carbonate.

The general chemical behaviour of casein resembles that of albumen. It contains a little less sulphur than albumen and fibrin.

Legumin, or *vegetable casein*, is found in peas, beans, and most leguminous seeds. If dried peas be crushed and digested for some time in warm water, a turbid liquid is obtained, holding starch in suspension; this is allowed to settle, the supernatant liquid precipitated by acetic acid, and the legumin purified from fat by washing with alcohol and ether. It closely resembles casein, its solution forming a pellicle when heated, and being coagulated by rennet. In composition, it differs somewhat from casein, containing about 1 per cent. more nitrogen, and only about half as much sulphur. When boiled with dilute sulphuric acid, legumin yields much less leucine than albumen and fibrin furnish, and very little tyrosine; but it gives more aspartic acid and *glutamic acid* ($C_3H_5.NH_2(CO_2H)_2$, homologous with aspartic acid).

Gluten is the tough, sticky substance which is left when flour is made into dough, tied up in muslin, and kneaded in water as long as any starch passes through. It speedily putrefies when exposed to the air, and dries up to a brittle, horny mass at 100° C. When fresh gluten is boiled with dilute alcohol, a portion is left undissolved, and has been named *vegetable fibrin*, as it forms a tough, elastic mass. It dissolves in very dilute HCl and in dilute alkalies, and is precipitated by acetic acid and by salts. When the alcoholic solution cools, it deposits white flakes of *gluten-casein*, and on adding water to the filtrate, *glutin*, or *gliadin*, is precipitated. These substances resemble legumin in composition, but contain twice as much sulphur.

567. PROTEIDS.—The albuminoids were formerly supposed to be derived from a primary source termed *protein*, and are often referred to as *protein compounds*, but the term proteid comprises certain animal substances which appear to have been formed from the albuminoids, and resemble them in their general reactions.

Keratin forms the chief part of horns, claws, nails, feathers, hair, and wool, and remains when these have been treated with all ordinary solvents. It is softened by long boiling with water, and is dissolved when heated with water under pressure. It swells up and gradually becomes soluble in strong alkalies and acetic acid, especially on boiling. It contains more sulphur than the albuminoids. *Fibroin* from silk, and *spongin* from sponge, are similar bodies.

Mucin is the substance which gives the viscous character to bile, saliva, and some other animal secretions, and to the slime of the snail. To prepare it, snails are cut up, triturated with sand to a pulp, boiled with water, filtered while hot, and precipitated by excess of acetic acid; the precipitated mucin is washed with weak acetic acid as long as the washings are precipitated by tannic acid, indicating peptone. Dry mucin is unaffected even by hot water. Moist mucin swells up in a remarkable manner in water, but does not dissolve; a little acid causes it to separate in flocks which do not easily dissolve in an excess of acid. Alkalies dissolve it, and acids reprecipitate it. Mucin dissolves in a strong solution of salt, and is precipitated again by water. Alcohol coagulates mucin into flocks. Acid solutions of mucin are not precipitated by potassium ferrocyanide (unlike albumen). Boiling dilute acids dissolve mucin, converting it into a substance having the properties of glucose and another which resembles albumen. The composition of mucin has not been well established; it contains the same elements as albumen, but much less nitrogen.

Nuclein is contained in the nuclei of pus-globules, in the blood-globules of birds and snakes, in yolk of egg, in brain, and in milk. It stands apart from other proteids, by containing about 2 per cent. of phosphorus in actual organic combination (and not as calcium phosphate, which so constantly accompanies the albuminoids). In extracting it, advantage is taken of its insolubility in the digestive fluids. Pus-globules are treated with warm alcohol, which removes lecithin, and afterwards with a pepsin solution made from extract of pig's stomach, and containing 1 per cent. of strong HCl. The insoluble residue consists of nuclein.

Pus-globules are obtained by treating the discharge, or the bandages to which it adheres, with a mixture of 1 part of a saturated solution of sodium sulphate and 9 parts of water, when the serum remains in solution, and the pus-globules sink and may be washed by decantation; if these be digested with cold dilute HCl and afterwards shaken with a mixture of ether and water, the nuclei remain as a fine powder at the bottom.

Nuclein is remarkable for its insolubility in all ordinary solvents; it appears to have an acid character, and dissolves in sodium carbonate or acetate, the solution in the latter giving precipitates with salts of zinc, copper, and lead. It is of considerable importance in the chemistry of physiology, since it appears to be the chief constituent of the cell-nucleus or cytoblast (*κύω, I hold; βλαστός, a sprout*).

Amyloid matter is a substance resembling albumen in composition, but was originally mistaken for starch, because it gives a brown-violet colour with iodine, and a violet or blue if previously treated with sulphuric acid. It occurs in certain diseased conditions of various organs, as in the liver, kidneys, spleen, and brain, and may be extracted from the minced matter by exhausting with water, alcohol, and alcohol containing hydrochloric acid, and afterwards with artificial gastric juice (pepsin and HCl) at 40° as long as anything dissolves. It is an amorphous substance resembling insoluble albumen in many of its properties.

568. BRAIN AND NERVOUS SUBSTANCE.—The brain and nerves contain a peculiar phosphorised fat which has been termed *lecithin*, and has the empirical formula $C_{42}H_{84}NPO_{9}$. It is a glycerin derivative, and its reactions show that it contains the group C_3H_5 (glyceryle), and probably the radicals of palmitic and oleic acids, and a phosphorised group, $N(CH_3)_3.C_2H_4(PO_2)O_2$, closely related to neurine, $N(CH_3)_3.C_2H_6O_2$ (p. 673). A variation in the fatty acid radicals gives rise to lecithins of different formulæ, which appear to be constant constituents of the cell-material of organised bodies, both animal and vegetable, and hence necessitate a constant supply of phosphorus in the food of plants and animals.

Lecithin may be prepared from the substance of the brain by exhausting it with ether, treating the residue with alcohol, and cooling the alcoholic solution in ice, when a mixture of lecithin and cerebrin is deposited. On treating this with ether, the lecithin is dissolved, and may be purified by evaporating the ether, redissolving in alcohol, adding an alcoholic solution of platinic chloride, and decomposing the platinum salt, $(C_{42}H_{83}NPO_{8}Cl)_2.PtCl_4$, with H_2S; on evaporating the filtrate, the lecithin is obtained as a fusible crystalline body, insoluble in water and sparingly soluble in cold alcohol and ether. It combines both with bases and acids. When boiled with acids or with potash or baryta, it yields neurine, phosphoglyceric acid, $C_3H_5(OH)_2 PO_2(OH)_2$, palmitic and oleic acids.

Cerebrin, obtained from brain as above described, is a white powder, which swells up like starch when boiled with water. It yields a substance resembling glucose when boiled with dilute acids. The formula of cerebrin, or *cerebric acid*, as it is sometimes called, appears to be $C_{17}H_{33}NO_3$. It is also found in pus-globules.

The so-called *protagon* appears to be a mixture of lecithin and cerebrin.

569. COLOURING MATTERS OF THE ANIMAL BODY.—The colouring matter contained in the red globules of arterial blood is called *oxyhæmoglobin*, and resembles albumen in composition, except that it contains only 0.4 per cent. of sulphur and 0.43 per cent. of iron. To extract it from blood, the fibrin is separated by whipping (p. 682), and the defibrinated blood is mixed with ten volumes of a solution containing 3 per cent. of common salt. This prevents the coagulation of the fibrin, and the red globules subside after a day or two; the clear liquid is poured off, and the globules shaken with water and an equal volume of ether, which dissolves the envelopes of the globules, and allows the colouring matter to pass into the water. The aqueous layer is separated, cooled in ice, one-fourth of its volume of alcohol added, and the cooling carried to − 5° C., when the oxyhæmoglobin crystallises out in forms which vary in different animals. That obtained from the blood of men, oxen, sheep, pigs, and rabbits is not easily obtained in crystals, the best for this purpose being the blood of dogs, guinea-pigs, hedgehogs, and rats. The crystals contain oxygen in a loosely combined form, which they evolve when exposed in a vacuum, especially if warmed, becoming thus converted into *hæmoglobin*, which again absorbs oxygen on exposure to air; this change is attended with production of a much brighter red colour, and with a difference in its action on transmitted light, for if white light be allowed to pass through the solution of oxyhæmoglobin contained in a test-tube placed before the slit of a spectroscope (p. 273), the green portion of the spectrum is seen to be crossed by two broad black bands, which are also seen when arterial blood is employed, whilst the solution of hæmoglobin exhibits only one band in the middle of the green, which is seen when

venous blood is employed. This difference in the *absorption spectrum* is best shown by reducing the solution of oxyhæmoglobin with a little ferrous sulphate, mixed with tartaric acid and ammonia in excess. The oxygen of oxyhæmoglobin is also displaced by passing hydrogen or carbon dioxide, hæmoglobin being left, and the colour changing from red to purple.

Oxyhæmoglobin, when shaken with carbonic oxide gas, parts with its oxygen and absorbs an equal volume of carbonic oxide, its colour changing to purple; the absorption-spectrum exhibits two dark bands, which are situated further from the sodium-line (D) and nearer to the blue of the spectrum than is the case with hæmoglobin. This is turned to account in cases of poisoning by carbonic oxide gas. The compound of hæmoglobin and carbonic oxide may be obtained in bluish-red, four-sided prisms. When solution of oxyhæmoglobin is heated above 70° C., it is decomposed into albumen, which coagulates, and another red colouring matter, termed hæmatin.

Hæmatin, $C_{34}H_{34}N_4FeO_5$, is formed when oxyhæmoglobin is decomposed by acids. If a solution of that substance, mixed with a little NaCl, is evaporated over sulphuric acid to a syrup, mixed with 15 times its volume of glacial acetic acid, and heated on a steam-bath for several hours, it yields, on cooling, flat rhombic prisms of hæmatin hydrochloride (formerly known as *hæmin*, or *blood-crystals*), of a dark, violet-red colour, and metallic lustre, containing single molecules of hæmatin and HCl. The formation of these crystals is employed for the identification of blood-stains, the suspected matter being placed on a microscope slide, a little sodium chloride added, and glacial acetic acid allowed to run under the cover-glass; on heating till bubbles appear, and cooling, the dark red hæmin crystals become visible.

Colouring matters of bile.—The chief of these is *bilirubin*, $C_{16}H_{18}N_2O_3$, which is accompanied by *bilifuscin*, $C_{16}H_{20}N_2O_4$, and *biliprasin*, $C_{16}H_{22}N_2O_5$. These may be extracted from gall-stones, in which they exist in combination with calcium. The powdered calculi are boiled with alcohol and ether to extract the cholesterin, and with dilute HCl to remove the lime. After washing and drying, the residue is boiled with chloroform, which extracts bilirubin and bilifuscin; the chloroform is distilled off and the residue boiled with alcohol, which dissolves the latter. The original residue, undissolved by chloroform, contains biliprasin, which may be extracted by boiling with alcohol.

Bilirubin crystallises from chloroform in dark-red prisms, insoluble in water and alcohol, but soluble in alkaline liquids, and imparting a yellow colour to a very large volume of solution. It appears to have acid properties. Its alkaline solutions absorb oxygen and become green, yielding a green precipitate of *biliverdin*, $C_{16}H_{20}N_2O_5$, on addition of an acid. Bilifuscin and biliprasin are obtained as very dark green amorphous bodies, insoluble in water. The alkaline solutions of the biliary colouring matters, when treated with nitric acid, yield successive tints of green, blue, violet, red, and yellow, which serve to indicate the presence of bile in other secretions.

The *colouring matters of urine* have received various names, but have not been established as definite chemical compounds.

ON SOME OF THE USEFUL APPLICATIONS OF THE PRINCIPLES OF ORGANIC CHEMISTRY.

DESTRUCTIVE DISTILLATION OF COAL.

570. Much of the extraordinary progress made by chemistry during the last half-century must be attributed to the introduction and great extension of the manufacture of coal-gas. No other branch of manufacture has brought into notice so many compounds not previously obtained from any other source, and, above all, offering, at first sight, so very little promise of utility, as to press urgently upon the chemist the necessity for submitting them to investigation.

Although many important additions to chemical knowledge have resulted from the labours of those who have engaged in devising the best methods of obtaining the coal-gas itself in the state best fitted for consumption, far more benefit has accrued to the science from investigations into the nature of the secondary products of the manufacture, the removal of which was the object to be attained in the purification of the gas.

Of the compounds of carbon and hydrogen, very little was known previously to the introduction of coal-gas; and although the liquid hydrocarbons composing coal-naphtha were originally obtained from other sources, the investigation of their chemical properties has been greatly promoted by the facility with which they may be obtained in large quantities from that liquid. The most important of these hydrocarbons, *benzole* or *benzene*, was originally procured from benzoic acid; but it would have been impossible for it to have fulfilled its present useful purposes unless it had been obtained in abundance as a secondary product in the manufacture of coal-gas; for, leaving out of consideration the various uses to which benzene itself is devoted, it yields the *nitrobenzene*, so much used in perfumery, and from this we obtain *aniline*, from which many of the most beautiful dyes are now prepared.

The *naphthalene* found so abundantly in coal-tar possesses a peculiar interest, as having formed the subject of the classical researches by which Laurent was led to propose the doctrine of substitution, which has since thrown so much light upon the constitution of organic substances.

We are also especially indebted to coal-tar for our acquaintance with the very interesting and rapidly extending class of volatile alkalies, of which the above-mentioned aniline is the chief representative, and for *phenic* or *carbolic acid*, from which are derived the large number of substances composing the phenyl series.

The retorts in which the distillation of coal is effected are made either of cast-iron or of fire-clay, generally having the form of a flattened cylinder, and arranged in sets of three or five, heated by the same coal fire (fig. 287). The coal is thrown on to the red-hot floor of the retort, as soon as the coke from the previous distillation has been raked out; the mouth of the retort is then closed with an iron plate luted with clay. An iron pipe rises from the upper side of the front of the retort projecting from the furnace, and is curved round at the upper extremity, which passes into the side of a much wider tube, called the *hydraulic main*, running above the furnaces, at right angles to the retorts, and receiving the tubes from all of them. This tube is always kept half full of the tar and water condensed from the gas, and below the surface of this liquid the delivery tubes from the retorts are allowed to dip, so that, although the gas can bubble freely through the liquid as it issues from the retort, none can return through the tube whilst the retort is open for the introduction of a fresh charge.

Exhausters are used in most gas-works, to prevent the pressure in the retort from exceeding that of the atmosphere, thus diminishing loss by leakage, and quickly removing the gas from the injurious effect of the hot retort.

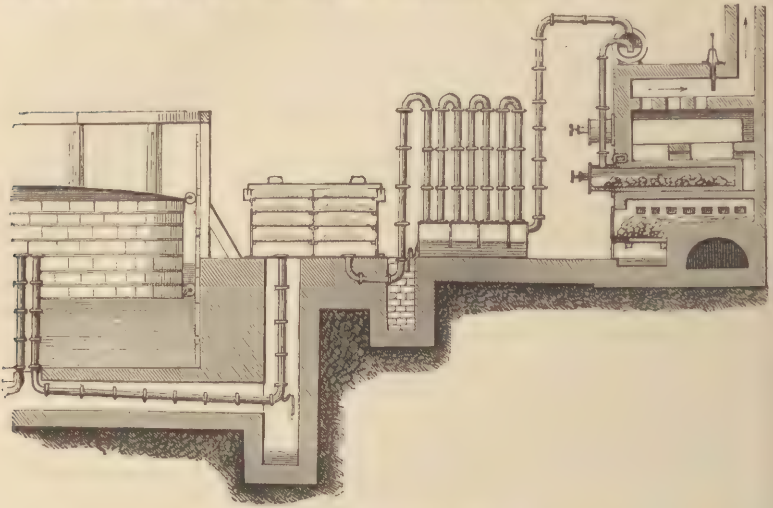

Fig. 287.—Manufacture of coal-gas.

The aqueous portion of the liquid deposited in the hydraulic main is known as the *ammoniacal liquor*, from its consisting chiefly of a solution of various salts of ammonium, the chief of which is the carbonate; sulphide, cyanide, and sulphocyanide of ammonium are also found in it.

From the hydraulic main the gas passes into the *condenser*, which is composed of a series of bent iron tubes kept cool either by the large surface which they expose to the air, or sometimes by a stream of cold water. In these are deposited, in addition to water, any of the volatile hydrocarbons and ammonium salts which may have escaped condensation in the hydraulic main. Even in the condenser the removal of the ammoniacal salts is not complete, so that it is usually necessary to pass the gas through a *scrubber* or case containing fragments of coke, over which a stream of water is allowed to trickle, in order to absorb the remaining ammoniacal vapours.

The *tar* which condenses in the hydraulic main is a very complex mixture, of which the following are some of the leading components :—

	Boiling Point.	Formula.	Sp. Gr.
NEUTRAL HYDROCARBONS.			
Liquid.			
Benzene	176° F.	C_6H_6	0.88
Toluene	230°	C_7H_8	0.87
Xylene	284°	C_8H_{10}	0.87
Isocumene* . . .	338°	C_9H_{12}	0.85
Solid.			
Naphthalene . . .	428°	$C_{10}H_8$	
Anthracene . . .	680°	$C_{14}H_{10}$	
Chrysene	...	$C_{18}H_{12}$	
Pyrene	...	$C_{16}H_{10}$	

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* *Benzene*, originally derived from *benzoic acid*; *toluene*, from balsam of *tolu*; *xylene*,

	Boiling Point.	Formula.	Sp. Gr.
ALKALINE PRODUCTS.			
Ammonia	...	NH_3	
Aniline	360°	C_6H_7N	1.02
Picoline	271°	C_6H_7N	0.96
Quinoline	462°	C_9H_7N	1.08
Pyridine	240°	C_5H_5N	
ACIDS.			
Carbolic acid . . .	370°	C_6H_6O	1.07
Kresylic " . . .	397°	C_7H_8O	
Rosolic " . . .	...	$C_{19}H_{14}O_3$	
Brunolic " . . .			
Acetic " . . .	243°	$C_2H_4O_2$	1.06

The gas is now passed through the *lime-purifier*, which is an iron box with shelves on which dry slaked lime is placed in order to absorb the carbonic acid gas and sulphuretted hydrogen, and the last portions of ammonia are removed by passing the gas through dilute sulphuric acid.

A great many other methods have been devised for the purification of the gas from sulphuretted hydrogen, but none appears to be so efficacious and economical as that which consists in passing the gas over a mixture of ferrous sulphate (green vitriol or copperas), slaked lime, and sawdust (which is employed to prevent the other materials from caking together). The lime decomposes the ferrous sulphate, forming calcium sulphate and ferrous hydrate—

$$FeSO_4 + Ca(HO)_2 = Fe(HO)_2 + CaSO_4.$$

The action of air upon the mixture soon converts the ferrous into ferric hydrate, which absorbs the sulphuretted hydrogen and the hydrocyanic acid, producing with the former ferrous sulphide, and with the latter Prussian blue or some similar compound. The calcium sulphate existing in this purifying mixture is useful in absorbing any vapour of ammonium carbonate from the gas, forming ammonium sulphate and calcium carbonate.*

The action of the sulphuretted hydrogen on the ferric oxide is represented by two equations (1) $Fe_2O_3 + H_2S = 2FeO + H_2O + S$; (2) $Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + S$; and the circumstance which especially conduces to the economy of the process is the facility with which the ferrous sulphide and oxide may be reconverted into the ferric oxide by mere exposure to the action of atmospheric oxygen; for $2FeS + O_3 = Fe_2O_3 + S_2$, thus reviving the power of the mixture to absorb sulphuretted hydrogen. Accordingly, if a small quantity of air be admitted into the purifier together with the gas, it reconverts the ferrous sulphide and oxide into ferric oxide, and the oxidation is attended with enough heat to convert into vapour any benzene which may have condensed in the purifying mixture, and of which the illuminating value would otherwise be lost. The same purifying mixture may thus be employed to purify a very large quantity of gas, until the separated sulphur has increased its bulk to an inconvenient extent, when it is distilled off in iron retorts. The various processes which have been devised for the removal of the carbon disulphide vapour are mentioned at page 216.

The purified gas is passed into the gasometers, from which it is supplied for consumption.

In the manufacture of coal gas, attention is requisite to the temperature at which the distillation is effected, for, if it be too low, the solid and liquid hydrocarbons will be formed in too great abundance, not only diminishing the volume of the gas, but causing much inconvenience by obstructing the pipes. On the other hand, if the retort be too strongly heated, the vapours of volatile hydrocarbons, as well as the olefiant gas and marsh gas, may undergo decomposition, depositing their carbon upon the sides of the retort, in the form of gas-carbon, and leaving their hydrogen to increase the volume and dilute the illuminating power of the gas.

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found among the products from *wood* (ξύλον); isocumene, isomeric with cumene, obtained from oil of *cummin*.

* Ferric hydrate, derived from various natural and artificial sources, is also employed for the purification of coal gas. Brown hæmatite (bog ore) is frequently employed.

These effects are well exemplified in the following analysis of the gas collected from Wigan cannel coal at different periods of the distillation :—

In 100 Volumes.	1st Hour.	5th Hour.	10th Hour.
Olefiant gas and volatile hydrocarbons .	13.0	7.0	
Marsh gas	82.5	56.0	20.0
Carbonic oxide	3.2	11.0	10.0
Hydrogen	...	21.3	60.0
Nitrogen	1.3	4.7	10.0

The increase of the carbonic oxide after the first hour must be attributed to the decomposition of the aqueous vapour by the carbon as the temperature rises, and the increase of the nitrogen may probably be ascribed to the decomposition of the ammonia into its elements at a high temperature.

Much advantage is said to be gained by mixing the coal with a certain proportion of lime, which diminishes the sulphur in the gas and increases the yield of ammonia.

One of the most useful of the secondary products of the coal-gas manufacture is the ammonia, and this process has been already noticed as a principal source of the ammoniacal salts found in commerce.

Next in the order of usefulness stands the coal-tar, which deserves attentive consideration, not only on that account, but because the extraction of the various useful substances from this complex mixture affords an excellent example of *proximate organic analysis*, that is, of the separation of an organic mixture into its immediate components.

For the separation of the numerous volatile substances contained in coal-tar, advantage is taken of the difference in their boiling points, which will be observed on examining the table at page 688.

A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown oily offensive liquid which collects upon the surface of the water. This is a mixture of the hydrocarbons which are lighter than water, viz., benzene, toluene, xylene, and isocumene, all having, as represented in the table at page 688, a specific gravity of about 0.85. 100 parts of the tar yield, at most, 10 parts of this *light oil.*

As the distillation proceeds, and the temperature rises, a yellow oil distils over, which is heavier than water, and sinks in the receiver. This oil, commonly called *dead oil*, is much more abundant than the light oil, amounting to about one-fourth of the weight of the tar, and contains those constituents of the tar which have a high specific gravity and boiling point, particularly naphthalene, aniline, quinoline, and carbolic acid. The proportion of naphthalene in this oil increases with the progress of the distillation, as would be expected from its high boiling point, so that the last portions of the oil which distil over become nearly solid on cooling. When this is the case, the distillation is generally stopped, and a black viscous residue is found in the retort, which constitutes *pitch*, and is employed for the preparation of Brunswick black and of asphalt for paving.

The light oil which first passed over is rectified by a second distillation, and is then sent into commerce under the name of *coal-naphtha*, a quantity of the heavy oil being left in the retort, the lighter oils having lower boiling points.

This coal-naphtha may be further purified by shaking it with sulphuric acid, which removes several of the impurities, whilst the pure naphtha collects on the surface when the mixture is allowed to stand. When this is again distilled it yields the *rectified coal-naphtha.*

This light oil, especially when distilled from cannel coal at a low temperature, contains, in addition to the hydrocarbons above enumerated, some belonging to the marsh gas series (C_nH_{2n+2}), and others more recently brought to light, belonging to a series the general formula of which is C_nH_{2n-2}; but these last appear to be acted on by the sulphuric acid, employed to remove the basic substances from the light oil, in such a manner that they are converted into polymeric hydrocarbons, having the general formula $C_{2n}H_{4n-4}$, of which the three following have been particularly examined :—

Formula.	Boiling Point.
$C_{12}H_{20}$	410° F.
$C_{14}H_{24}$	464°
$C_{16}H_{28}$	536°

The hydrocarbons C_6H_{10}, C_7H_{12}, and C_8H_{14}, from which these appear to have been formed by the action of sulphuric acid, would evidently be the higher homologues of acetylene, C_2H_2.

The distillation of cannel coal, and of various minerals nearly allied to coal, at low temperatures, is now extensively carried on for the manufacture of paraffin and paraffin oil (see *Paraffin*).

Coal-tar dyes.—The first dye ever manufactured from aniline on a large scale was that known as *mauve*,* or *aniline purple*, which is obtained by dissolving aniline in diluted sulphuric acid, and adding solution of bichromate of potash, when the liquid gradually becomes dark-coloured, and deposits a black precipitate, which is filtered off, washed, boiled with coal-naphtha to extract a brown substance, and afterwards treated with hot alcohol, which dissolves the mauve. The chemical change by which the aniline has been converted into this colouring-matter cannot at present be clearly traced, but the basis of the colour has been found to be a substance which has the composition $C_{27}H_{24}N_4$, and has been termed *mauvéine*. It forms black shining crystals, resembling specular iron ore, which dissolve in alcohol, forming a violet solution, and in acids, with production of the purple colour. Mauvéine combines with the acids to form salts; its alcoholic solution even absorbs carbonic acid gas. The *hydrochlorate of mauvéine*, $C_{27}H_{24}N_4.2HCl$, forms prismatic needles with a green metallic lustre.

Very brilliant red dyes are obtained from commercial aniline by the action of carbon tetrachloride, stannic chloride, ferric chloride, cupric chloride, mercuric nitrate, corrosive sublimate, and arsenic acid. It will be noticed that all these agents are capable of undergoing reduction to a lower state of oxidation or chlorination, indicating that the chemical change concerned in the transformation of aniline into aniline-red is one in which the aniline is acted on by oxygen or chlorine.

The easiest method of illustrating the production of aniline-red, on the small scale, consists in heating a few drops of aniline in a test-tube with a fragment of corrosive sublimate (mercuric chloride), which soon fuses and acts upon the aniline to form an intensely red mass composed of aniline-red, calomel, and various secondary products. By heating this mixture with alcohol, the red dye is dissolved, and a skein of silk or wool dipped into the liquid becomes dyed of a fine red, which is not removed by washing.

On the large scale, *magenta* (as aniline-red is commonly termed) is generally prepared by heating aniline to about 320° F. with arsenic acid, when a dark semi-solid mass is obtained, which becomes hard and brittle on cooling, and exhibits a green metallic reflection. This mass contains, in addition to aniline-red, several secondary products of the action, and arsenious acid. On boiling it with water, a splendid red solution is obtained, and a dark resinous or pitchy mass is left. If common salt be added to the red solution as long as it is dissolved, the bulk of the colouring matter is precipitated as a resinous mass, which may be purified from certain adhering matters by drying and boiling with coal-naphtha. The red colouring matter is the arsenate of a *colourless* organic base, which has been called *rosaniline*, and has the composition $C_{20}H_{19}N_3.H_2O$. If the red solution of arsenate of rosaniline be decomposed with calcium hydrate suspended in water, a pinkish precipitate is obtained, which consists of rosaniline mixed with calcium arsenate, and the solution entirely loses its red colour.

By treating the precipitate with a small quantity of acetic acid, the rosaniline is converted into *rosaniline acetate* ($C_{20}H_{19}N_3,C_2H_4O_2$), forming a red solution, which may be filtered off from the undissolved calcium arsenate. On evaporating the solution to a small bulk, and allowing it to stand, the acetate is obtained in crystals which exhibit the peculiar green metallic lustre of the wing of the rose-beetle, characteristic of the salts of rosaniline. This salt is the commonest commercial form of magenta; its colouring power is extraordinary, a very minute particle imparting a red tint to a large volume of water. Silk and wool easily extract the whole of the colouring matter from the aqueous solution, becoming dyed a fast and brilliant crimson; cotton and linen, however, have not so strong an attraction for it, so that if a pattern be worked in silk upon a piece of cambric, which is then immersed in a solution of magenta and afterwards washed in hot water, the colour will be washed out of the cambric; but the red silk pattern will be left.

If a boiling solution of rosaniline acetate be mixed with excess of ammonia, the bulk of the rosaniline will be precipitated, but if the solution be filtered while hot, it deposits colourless needles of rosaniline, which become red when exposed to the air, from absorption of carbonic acid, and formation of the red rosaniline carbonate.

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* French for marshmallow, in allusion to the colour of the flower.

Water dissolves but little rosaniline; alcohol dissolves it abundantly, forming a deep red solution. Rosaniline forms two classes of salts with acids, those with 1 molecule of acid (*monacid* salts) being crimson, and those with three molecules (*triacid* salts) having a brown colour. Thus, if colourless rosaniline be dissolved in a little dilute hydrochloric acid, a red solution is obtained, which contains the monacid rosaniline hydrochlorate, $C_{20}H_{19}N_3.HCl$; but if an excess of hydrochloric acid be added, the red colour disappears, and a brown solution is obtained, from which the triacid hydrochlorate, $C_{20}H_{19}N_3.3HCl$, may be crystallised in brown red needles.

For experimental illustration of the properties of rosaniline, the liquid obtained by boiling a solution of the acetate with a slight excess of lime diffused in water, and filtering while hot, is very well adapted. The solution has a yellow colour, and may be preserved in a stoppered bottle without alteration. If air be breathed into it through a tube, the liquid becomes red from production of rosaniline carbonate. Characters painted on paper with a brush dipped in the solution are invisible at first, but gradually acquire a beautiful rose colour.

When the red solution of rosaniline hydrochlorate is slightly acidified with hydrochloric acid and placed in contact with zinc, the solution becomes colourless, the rosaniline acquiring 2 atoms of hydrogen, and becoming *leucaniline* (from λευκὸς, *white*), $C_{20}H_{21}N_3$, the hydrochlorate of which ($C_{20}H_{21}N_3.3HCl$) forms a colourless solution. Oxidising agents reconvert the leucaniline into rosaniline. It has been observed that *pure* aniline does not yield aniline red when heated with corrosive sublimate or arsenic acid, it being necessary that it should contain another organic base, *toluidine* (C_7H_9N), which is derived from toluene (C_7H_8) in the same way in which aniline is derived from benzene. Since the benzene obtained from coal-naphtha almost invariably contains toluene, the aniline obtained from it is very seldom free from toluidine. If the aniline be prepared with benzene derived from benzoic acid, and therefore free from toluene, no red is obtained. A mixture of 70 parts of toluidine with 30 of aniline is said to answer best for the preparation of the red and violet colouring matters. Such a mixture would contain 2 molecules of toluidine (C_7H_9N) and 1 of aniline (C_6H_7N), or $C_{20}H_{25}N_3$, only requiring the removal of H_6 by an oxidising agent to yield rosaniline, $C_{20}H_{19}N_3$.

Aniline-yellow, or *chrysaniline* (from χρύσεος, *golden*), is found among the secondary products obtained in the preparation of aniline-red. It forms a bright yellow powder, resembling chrome-yellow, and having the composition $C_{20}H_{17}N_3$. It is nearly insoluble in water, but dissolves in alcohol. Chrysaniline has basic properties, and dissolves in acids, forming salts. On dissolving it in diluted hydrochloric acid, and mixing the solution with the concentrated acid, a scarlet crystalline precipitate of *chrysaniline hydrochlorate* ($C_{20}H_{17}N_3.2HCl$) is obtained, which is insoluble in strong hydrochloric acid, but very soluble in water. A characteristic feature of chrysaniline is the sparing solubility of its nitrate. Even from a dilute solution of the hydrochlorate, nitric acid precipitates chrysaniline nitrate ($C_{20}H_{17}N_3.HNO_3$) in ruby-red needles.

Aniline-blue is produced when a salt of rosaniline (the commercial acetate, for example) is boiled with an excess of aniline, which converts the rosaniline ($C_{20}H_{19}N_3$) into *triphenylic rosaniline* ($C_{20}H_{16}(C_6H_5)_3N_3$), which may be regarded as having been formed by the introduction of 3 atoms of the hydrocarbon radical *phenyle* (C_6H_5) in place of 3 atoms of hydrogen, the latter having been evolved in the form of ammonia—

$$\underset{\text{Rosaniline hydrochlorate.}}{C_{20}H_{19}N_3HCl} + \underset{\text{Aniline.}}{3[(C_6H_5)H_2N]} = \underset{\text{Triphenylic rosaniline hydrochlorate.}}{C_{20}H_{16}(C_6H_5)_3.N_3.HCl} + 3NH_3.$$

The hydrochlorate is an ordinary commercial form of aniline-blue; it has a brown colour, refuses to dissolve in water, but yields a fine blue solution in alcohol. If it be dissolved in an alcoholic solution of ammonia, the addition of water causes a white precipitate of the hydrated base, triphenylic rosaniline, $C_{20}H_{16}(C_6H_5)_3N_3.H_2O$, which becomes bluish when washed and dried.

Just as rosaniline yields leucaniline when acted on with nascent hydrogen, so triphenylic rosaniline yields triphenylic leucaniline, $C_{20}H_{18}(C_6H_5)_3N_3$; this is not basic like leucaniline, but a neutral colourless substance, which is reconverted into blue by oxidising agents. Compounds corresponding to triphenylic rosaniline, but containing methyle, ethyle, or amyle in place of phenyle, are obtained by digesting rosaniline with the iodides of these radicals, at a high temperature, in sealed tubes. Thus, by the action of ethyle iodide (C_2H_5I) upon rosaniline, a blue crystalline body, insoluble in water, but soluble in alcohol, is obtained, which is a compound of ethyle iodide with triethylic rosaniline; $C_{20}H_{16}(C_2H_5)_3N_3$.

$$\underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 4C_2H_5I = \underset{\text{Tri-ethyl-rosaniline ethyl-iodate.}}{C_{20}H_{16}(C_2H_5)_3N_3.C_2H_5I} + 3HI.$$

Aniline-violet is formed in a similar manner with methyle iodide. Other compounds have been obtained from aniline, presenting almost every variety of colour. A *green* dye is prepared by the action of a mixture of hydrochloric acid and potassium chlorate upon aniline, and under particular conditions a *black* may be obtained with the same agents. Another green has been made by acting upon magenta with aldehyd.

When a solution of rosaniline acetate is treated with potassium cyanide, it gradually loses its red colour, and deposits a white crystalline precipitate of a base which has been termed *hydrocyan-rosaniline*, having the formula $C_{21}H_{20}N_4$, and containing the elements of rosaniline and hydrocyanic acid; but this acid cannot be detected in it by the ordinary tests, leading to the belief that the new base should be regarded as leucaniline ($C_{20}H_{21}N_3$), in which one atom of hydrogen is replaced by cyanogen ($C_{20}H_{20}(CN)N_3$). The hydrocyan-rosaniline is almost insoluble in water, and sparingly soluble in boiling alcohol. When precipitated from its salts by adding an alkali, it becomes pink on exposure to sunshine.

DYEING AND CALICO-PRINTING.

571. The object of the dyer being to fix certain colouring matters permanently in the fabric, his processes would be expected to vary with the nature of the latter and of the colour to be applied to it. In order that uniformity of colour and its perfect penetration into the fibre may be obtained, it is evident that the colouring matter must always be employed in a state of solution; and it must be rendered *fast*, or not removable by washing, by assuming an insoluble condition in the fibre.

The simplest form of dyeing is that in which the fibre itself forms an insoluble compound with the colouring matter. Thus, if a skein of silk be immersed in a solution of indigo in sulphuric acid, it removes the whole of the colouring matter from the liquid, and may then be washed with water without losing colour; but if the same experiment be tried with cotton, the indigo will not be withdrawn from the solution, and when the cotton has been well squeezed and rinsed with water, it will become white again. It may be stated generally, that the animal fabrics (silk and wool) will absorb and retain colouring matters with much greater facility than vegetable fabrics (cotton and linen). In the absence of so powerful an attraction between the fibre and the colouring matter, it is usual to impregnate the fabric with a *mordant* or substance having an attraction for the colour, and capable of forming an insoluble combination with it, so as to retain it permanently attached to the fabric. Thus, if a piece of cotton be boiled in a solution of acetate of alumina, the alumina will be precipitated in the fibre; and if the cotton be then soaked in solution of cochineal or of logwood, the red colouring matter will form an insoluble compound (or *lake*) with the alumina, and the cotton will be dyed of a fast red colour.

Another method of fixing the colour in the fabric consists in impregnating the latter with two or more liquids in succession, by the admixture of which the colour may be produced in an insoluble state. If a piece of any stuff be soaked in solution of ferric chloride, and afterwards in potassium ferrocyanide, the Prussian blue which is precipitated in the fibre will impart a fast blue tint.

An indispensable preliminary step to the dyeing of any fabric is the removal of all natural grease or colouring matter, which is effected by processes varying with the nature of the fibre, and is preceded, in the cases of cotton and woollen materials which are to receive a pattern, by certain operations of shaving and singeing for removing the short hairs from the surface.

From linen and cotton, the extraneous matters (such as grease and resin) are generally removed by weak solutions of carbonate of potassium or of sodium, and the fabrics are afterwards bleached by treatment with chloride of lime (page 161). But since the fibres of silk and wool are much more easily injured by alkalies and by chlorine, greater care is requisite in cleansing them. Silk is boiled with a solution of white soap to remove the *gum*, as it is technically termed; but the natural grease is extracted from wool by soaking at a moderate temperature in a weak bath either of soap or of ammoniacal (putrefied) urine. Both silk and wool are bleached by sulphurous acid (page 198).

Among the *red dyes* the most important are *madder*, *alizarine*, *Brazil wood*, *cochineal*, *lac*, and the *aniline reds*.

In dyeing red with madder or Brazil wood, the linen, cotton, or wool is first mordanted by boiling in a solution containing alum and bitartrate of potash, when it combines with a part of the alumina, and on plunging the stuff into a hot infusion of madder, the colouring matter forms an insoluble combination with that earth.

To dye Turkey-red, the stuff is also mordanted with alum, but has previously to undergo several processes of treatment with oil and with galls, the necessity of which is satisfactorily established in practice, though it is not easy to explain their action. The colour is finally brightened by boiling the stuff with chloride of tin.

Woollen cloth is dyed scarlet with lac or cochineal, having been first mordanted by boiling in a mixture of perchloride of tin and bitartrate of potash.

The aniline colours (see page 691) are employed for dyeing silk and wool, either without any mordant or with the help of albumen.

Blues are generally dyed with *indigo* (page 667), or with *Prussian blue;* in the latter case the stuff is steeped successively in solutions of a salt of peroxide of iron and of potassium ferrocyanide. *Aniline blue* is also much employed for silk and woollen fabrics.

The principal *yellow dyes* are *weld*, *quercitron*, *fustic*, *annatto*, *chrysaniline*, and *lead chromate*. For the first four colouring matters aluminous mordants are generally applied. Lead chromate is produced in the fibre of the stuff, which is soaked for that purpose, first in a solution of acetate or nitrate of lead, and then in potassium chromate. Carbazotic or *picric acid* (page 540) is also sometimes employed as a yellow dye.

In dyeing *blacks* and *browns*, the stuffs are steeped first in a bath containing some form of tannin (page 525), such as infusion of *galls*, *sumach*, or *catechu*, and afterwards in a solution of a salt of *iron*, different shades being produced by the addition of indigo, of copper sulphate, &c.

The art of *calico-printing* differs from that of dyeing, in that the colour is required to be applied only to certain parts of the fabric so as to produce a pattern or design either of one or of several colours.

A common method of printing a coloured pattern upon a white ground consists in impressing the pattern by passing the stuff under a roller, to which an appropriate mordant thickened with British gum (page 652) is applied. The stuff is then *dunged*, *i.e.*, drawn through a mixture of cow-dung and water, which appears to act by removing the excess of the mordant, and afterwards immersed in the hot dye-bath, when the colour becomes permanently fixed to the mordanted device, but may be removed from the rest of the stuff by washing.

If the pattern be printed with a solution of acetate of iron, and the stuff immersed in a madder-bath, a lilac or black pattern will be obtained according to the strength of the mordant employed. By using acetate of alumina as a mordant, the madder-bath would give a red pattern.

A process which is the reverse of this is sometimes employed, the pattern being impressed with a *resist*, that is, a substance which will prevent the stuff from taking the colour in those parts which have been impregnated with it. For example, if a pattern be printed with thickened tartaric or citric acid, and the stuff be then passed through an aluminous mordant, the pattern will refuse to take up the alumina, and subsequently the colour from the dye-bath. Or a pattern may be printed with nitrate of copper, and the stuff passed through a bath of reduced indigo (page 668), when the nitrate of copper will oxidise the indigo, and, by converting it into the blue insoluble form, will prevent it from sinking into the fibre of those parts to which the nitrate has been applied, whilst elsewhere the fibre, having become impregnated with the white indigo, acquires a fast blue tint when exposed to the air.

Sometimes the stuff is uniformly dyed, and the colour discharged in order to form the pattern. A white pattern is produced upon a red (madder) or blue (indigo) ground by printing with a thickened acid discharge, and passing the stuff through a weak bath of chloride of lime, which removes the colour from those parts only which were impregnated with the acid (page 161). By adding lead nitrate to the acid discharge, and finally passing the stuff through solution of potassium chromate, a yellow pattern (lead chromate) may be obtained upon the madder red ground. By applying nitric acid as a discharge, a yellow pattern may be obtained upon an indigo ground (page 135).

Very brilliant designs are produced by mordanting the stuff in a solution of stannate of potassium or sodium (page 364), and immersing it in dilute sulphuric acid, which precipitates the stannic acid in the fibre.

When the thickened colouring matters are printed on in patterns and *steamed*, an insoluble compound is formed between the colour and the stannic acid.

It is evident that by combining the principles of which an outline has just been given, the most varied parti-coloured patterns may be printed.

TANNING.

572. When infusion of nut-galls is added to a solution of gelatin, the latter combines with the tannic acid, and a bulky precipitate is obtained. If a piece of skin, which has the same composition as gelatin, be placed in the infusion of nut-galls, it will absorb the whole of the tannic acid, and become converted into leather, which is much tougher than the raw skin, less permeable by water, and not liable to putrefaction.

The first operation in the conversion of hides into leather, after they have been cleansed, consists in soaking them for three or four weeks in pits containing lime and water, which saponifies the fat and loosens the hair. The same object is sometimes attained by allowing the hides to enter into putrefaction, when the resulting ammonia has the same effect as the lime. The loosened hair having been scraped off, the hides are soaked for twelve hours in water containing $\frac{1}{1000}$th of sulphuric acid, which removes adhering lime, and opens the pores of the skin, so as to fit it to receive the tanning liquid.

The tanning material generally employed for hides is the infusion of oak bark, which contains *querci-tannic acid*, very similar in properties to tannic acid. The hides are soaked in an infusion of oak bark for about six weeks, being passed in succession through several pits, in which the strength of the infusion is gradually increased. They are then packed in another pit with alternate layers of coarsely ground oak bark; the pit is filled with water and left at rest for three months, when the hides are transferred to another pit and treated in the same way; but, of course, the position of the hides will be now reversed—that which was uppermost, and in contact with the weakest part of the tanning liquor, will now be at the bottom. After the lapse of another three months the hide is generally found to be tanned throughout, a section appearing of a uniform brown colour. It has now increased in weight from 30 to 40 per cent. The chemical part of the process being now completed, the leather is subjected to certain mechanical operations to give it the desired texture. For tanning the thinner kinds of leather, such as morocco, a substance called *sumach* is used, which consists of the ground shoots of the *Rhus coriaria*, and contains a large proportion of tannic acid.

Morocco leather is made from goat and sheep skins, which are denuded of hair by liming in the usual way, but the adhering lime is afterwards removed by means of a bath of sour bran or flour. In order to tan the skin so prepared, it is sewn up in the form of a bag, which is filled with infusion of sumach, and allowed to soak in a vat of the infusion for some hours. A repetition of the process, with a stronger infusion, is necessary; but the whole operation is completed in twenty-four hours. The skins are now washed and dyed, except in the case of red morocco, which is dyed before tanning, by steeping it first in alum or chloride of tin, as a mordant, and afterwards in infusion of cochineal. Black morocco is dyed with acetate of iron, which acts upon the tannic acid. The aniline dyes are now much employed for dyeing morocco.

The *kid* of which gloves are made is not actually tanned, but submitted to an elaborate operation called *tawing*, the chief chemical features of which are the removal of the excess of lime,* and opening the pores of the skin by means of a sour mixture of bran and water, in which lactic acid is the agent; and the subsequent impregnation of the porous skin with aluminium chloride, by steeping it in a hot bath containing alum and common salt. The skins are afterwards softened by kneading in a mixture containing alum, flour, and the yolks of eggs.

* Polysulphides of sodium and calcium are sometimes employed for removing the hair.

The putrefaction of the skin is as effectually prevented by the aluminium chloride as by tanning.

Wash-leather and *buckskin* are not tanned, but *shamoyed*, which consists in sprinkling the prepared skins with oil, folding them up, and *stocking* them under heavy wooden hammers for two or three hours. When the grease has been well forced in, they are exposed in a warm atmosphere, to promote the drying of the oil by absorption of oxygen (page 697). These processes having been repeated the requisite number of times, the excess of oil is removed by a weak alkaline bath, and the skins are dried and rolled. The buff colour of wash-leather is imparted by a weak infusion of sumach.

Parchment is made by stretching lamb or goat skin upon a frame, removing the hair by lime, and scraping, as usual, and afterwards rubbing with pumice-stone, until the proper thickness is acquired.

OILS AND FATS.

573. A very remarkable feature in the history of the fats is the close resemblance in chemical composition and properties which exists between them, whether derived from the vegetable or the animal kingdom. They all contain two or more neutral substances which furnish glycerin when saponified, together with some of the acids of the acetic series or of series closely allied to it.

One of the most useful vegetable fatty matters is *palm oil*, which is extracted by boiling water from the crushed fruit of the *Elais guineensis*, an African palm. It is a semi-solid fat, which becomes more solid when kept, since it then undergoes a species of fermentation, excited apparently by an albuminous substance contained in it, in consequence of which the palmitin ($C_{51}H_{98}O_6$) is converted into glycerin and palmitic acid. The bleaching of palm oil is effected by the action of a mixture of sulphuric or hydrochloric acid and potassium dichromate, which oxidises the yellow colouring matter.

Cocoa-nut oil is also semi-solid, and is remarkable for the number of acids of the acetic series which it yields when saponified, viz., caproic, caprylic, rutic, lauric, myristic, and palmitic.

These fats are chiefly used in the manufacture of soap and candles.

Salad oil, or *sweet oil* (olive oil), is obtained by crushing olives, and an inferior kind which is used for soap is obtained by boiling the crushed fruit with water. When exposed to a temperature of about 32° F. a considerable portion of the oil solidifies; this solid portion is generally called *margarin*, ($C_{54}H_{104}O_6$); it is much less soluble in alcohol than stearin, though more so than palmitin. When saponified, margarin yields glycerin and *margaric acid* ($C_{17}H_{34}O_2$). This acid appears to be really composed of stearic and palmitic acids, into which it may be separated by repeated crystallisation from alcohol, when the palmitic acid is left in solution. The fusing point of margaric acid is 140° F., that of stearic being 159°, and that of palmitic, 144°, but a mixture of ten parts of palmitic with 1 part of stearic acid fuses at 140°.

That portion of the olive oil which remains liquid below 32° consists of *olein* ($C_{57}H_{104}O_6$), and forms nearly three-fourths of its weight.

It is well known that salad oil becomes rancid and exhales a disagreeable odour after being kept for some time. This appears to be due to a fermentation similar to that noticed in the case of palm oil, originally started by the action of atmospheric oxygen upon albuminous matters present in the oil; the neutral fatty matters are thus partly decomposed, as in saponification; their corresponding acids being liberated, and giving rise (in the case of the higher members of the acetic series, such as caproic and valerianic) to the disagreeable odour of rancid oil. By boiling the altered oil with water, and afterwards washing it with a weak solution of soda, it may be rendered sweet again.

Almond oil, extracted by a process similar to that employed for olive oil, is also very similar in composition; but *colza oil*, obtained from the seeds of the *Brassica oleifera*, contains only half its weight of oleine, and hence solidifies more readily than the others.

Colza oil is largely used for burning in lamps, and undergoes a process of purification from the mucilaginous substances which are extracted with it from the seed, and leave a bulky carbonaceous residue when subjected to destructive distillation in the wick of the lamp. To remove these, the oil is agitated with about 2 per cent. of oil of vitriol, which carbonises the mucilaginous substances, but leaves the oil untouched. When the carbonaceous flocks have subsided, the oil is drawn off, washed to remove the acid, and filtered through charcoal.

Linseed oil, obtained from the seeds of the flax plant, is much richer in olein than any of the foregoing, exhibiting no solidification till cooled to 15° or 20° F. below the freezing-point. It exhibits, however, in a far higher degree, a tendency to become solid when exposed to the air, which has acquired for it the name of a *drying oil*, and renders it of the greatest use to painters. This solidification is attended with absorption of oxygen, which takes place so rapidly in the case of linseed oil, that spontaneous combustion has been known to take place in masses of rag or tow which have been smeared with it.*

The tendency of linseed oil to solidify by exposure is much increased by heating it with about $\frac{1}{20}$th of litharge, or $\frac{1}{15}$th of black oxide of manganese; these oxides are technically known as *dryers*, and oil so treated is called *boiled linseed oil*. The action of these metallic oxides is not well understood.

The strong drying tendency of linseed oil is supposed to be due to a peculiarity in the olein, which is said not to be ordinary olein, but to furnish a different acid, *linoleic acid*, when saponified. When linseed oil is exposed for some time to a high temperature, it becomes viscous and treacly, and is used in this state for the preparation of printing ink. If the viscous oil be boiled with dilute nitric acid, it is converted into *artificial caoutchouc*, which is used in the manufacture of surgical instruments. This property appears to be connected with the drying qualities of the oil.

Castor oil, obtained from the seeds of *Ricinus communis*, also yields a peculiar acid when saponified, termed *ricinoleic* ($H.C_{18}H_{33}O_3$), containing one more atom of oxygen than oleic acid, which it much resembles. The destructive distillation of castor oil yields *œnanthic acid* ($H.C_7H_{13}O_2$) and *œnanthole*, or *œnanthic aldehyd* ($C_7H_{14}O$), and by distilling it with caustic potash, caprylic alcohol ($C_8H_{18}O$) is obtained. As in the case of olive oil, the *cold drawn* castor oil, which is expressed from the seeds without the aid of heat, is much less liable to become rancid. Castor oil is much more soluble in alcohol than any other of the fixed oils.

The various *fish oils*, such as seal and whale oil, also consist chiefly of olein, and appear to owe their disagreeable odour to the presence of certain volatile acids, such as valerianic.

Cod-liver oil appears to contain, in addition to olein and stearin, a small quantity of *acetin* ($C_9H_{14}O_6$), which yields acetic acid and glycerin when saponified. Some of the constituents of bile have also been traced in it, as well as minute quantities of iodine and bromine.

574. *Butter* contains about two-thirds of its weight of solid fat, which consists in great part of margarin (see page 696), but contains also *butine*, which yields glycerin and *butic acid* ($H.C_{20}H_{39}O_2$) when saponified. The liquid portion consists chiefly of olein. Butter also contains small quantities of butyrin, caproin, and caprin, which yield, when saponified, glycerin and butyric ($H.C_4H_7O_2$), caproic ($H.C_6H_{11}O_2$), and capric ($H.C_{10}H_{19}O_2$) acids, distinguished for their disagreeable odour.

Fresh butter has very little odour, being free from these volatile acids, but if kept for some time, especially if the casein of the milk has been imperfectly separated in its preparation, spontaneous resolution of these fats into glycerin and the volatile disagreeable acids takes place. By salting the butter this change is in great measure prevented.

The fat of the sheep and ox (*suet*, or, when melted, *tallow*) consists chiefly of stearin, whilst in that of the pig (*lard*) olein predominates to about the same extent as in butter. Margarin (or palmitin ?) is also present in these fats. *Benzoated lard* contains some gum benzoin, which prevents it from becoming rancid.

Human fat contains chiefly olein and margarin (or, if we do not admit the independent existence of the latter, palmitin and stearin).

575. *Sperm oil*, which is expressed from the spermaceti found in the brain of the sperm whale, owes its peculiar odour to the presence of a fat which has been called *phocenin*, but which appears to be *valerin*, as it yields glycerin and valerianic acid ($H.C_5H_9O_2$) when saponified.

The beautiful solid crystalline fat, known as *spermaceti* or *cetine*, differs widely from the ordinary fatty matters, for when saponified (which is not easily effected), it yields no glycerin, but in its stead another alcohol, termed *ethal* ($C_{16}H_{34}O$), which is a white crystalline solid, capable of being distilled without decomposition.

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* During the oxidation, a volatile compound is formed which resembles acroleine in smell, and colours unsized paper brown. It has been suggested that the brown colour and musty smell of old books may be due to the oxidation of the oil in the printing-ink.

The soap prepared from spermaceti, when decomposed by an acid, yields palmitic acid ($H.C_{16}H_{31}O_2$) (formerly called *ethalic acid*), to which ethal is the corresponding alcohol.

Ambergris, used in perfumery, is a fatty substance found in the intestines of the spermaceti whale. Boiling alcohol extracts from it about 80 per cent. of *ambrein*.

Chinese wax, the produce of an insect of the Cochineal tribe, is analogous in its chemical constitution to spermaceti. When saponified by fusion with caustic potash, it yields *cerotine*, or *cerylic alcohol* ($C_{27}H_{55}.HO$), corresponding to ethal, and *cerotic acid* ($H.C_{27}H_{53}O_2$), corresponding to palmitic acid. Cerotic acid is also contained in ordinary bees' wax, from which it may be extracted by boiling alcohol, and crystallised as the solution cools. It forms about two-thirds of the weight of the wax. Cerotic acid is found among the products of oxidation of paraffin by chromic acid.

Bees' wax also contains about one-third of its weight of *myricin* ($C_{46}H_{92}O_2$), a substance analogous to spermaceti, which yields, when saponified, palmitic acid and *melissin* ($C_{30}H_{61}.HO$), an alcohol corresponding to ethal. The colour, odour, and tenacity of bees' wax appear to be due to the presence of a greasy substance called *cerolein*, which forms about $\frac{1}{20}$th of the wax, and has not been fully examined. The *tree-wax* of Japan is said to be pure palmitin.

Wax is bleached for the manufacture of candles, by exposing it in thin strips or ribands to the oxidising action of the atmosphere, or by boiling it with nitrate of soda and sulphuric acid. Chlorine also bleaches it, but displaces a portion of the hydrogen in the wax, taking its place and causing the evolution of hydrochloric acid vapours when the wax is burnt.

The following table includes the principal fatty bodies and their corresponding acids, with their fusing points:—

Neutral Fats.	Formula.	Chief Source.	Fusing Point, Fahr.	Fatty Acids.	Formula.	Fusing Point, Fahr.
Stearin	$C_{57}H_{110}O_6$	Tallow	125° to 157°	Stearic	$C_{18}H_{36}O_2$	159°
Palmitin	$C_{51}H_{98}O_6$	Palm oil	114° to 145°	Palmitic	$C_{16}H_{32}O_2$	144°
Margarin	$C_{54}H_{104}O_6$	Olive oil	116°	Margaric	$C_{17}H_{34}O_2$	140°
Olein	$C_{57}H_{104}O_6$	,,	Below 32°	Oleic	$C_{18}H_{34}O_2$	40°
Cetin	$C_{32}H_{64}O_2$	Spermaceti	120°	Palmitic	$C_{16}H_{32}O_2$	144°
Myricin	$C_{46}H_{92}O_2$	Bees' wax	162°	,,		

CHEMISTRY OF SOAP.

576. The manufacture of soap affords an excellent instance of a process which was in use for centuries before anything was known of the principles upon which it is based, for it was not till the researches of Chevreul were published, in 1813, that any definite ideas were entertained with respect to the composition of the various fats and oils from which soaps are made.

The investigations of Chevreul are conspicuous among the labours which have contributed in so striking a manner to the rapid advancement of chemistry during the present century; undertaken when the chemistry of organic substances had scarcely advanced beyond the dignity of an art, when the principles of classification were almost entirely empirical, and hardly any research had been published which would serve as a model, these researches reflect the remarkable sagacity and accuracy of their author.

The sense of our obligation to this eminent chemist is further increased, when we remember that the ultimate analysis of organic substances was then effected by a very difficult and laborious process, whilst the doctrine of combining proportions was so imperfectly understood, that it could afford but little assistance in confirming or interpreting the results of analysis.

All soaps result from the action of the alkalies upon the oils and fats.

In the manufacture of soap, potash and soda are the only alkalies employed, the former for soft, the latter for hard soaps.

The fatty matters employed by the soap-maker are chiefly tallow, palm oil, cocoa-nut oil, and kitchen stuff, for hard soaps, and seal oil and whale oil for soft soaps.

In the manufacture of hard soap, the alkali is prepared by decomposing or *caustifying* sodium carbonate (soda-ash) with slaked lime, $Na_2CO_3 + Ca(HO)_2 = CaCO_3 + 2NaHO$, the clear solution of sodium hydrate, or *soda-ley*, being drawn off from the insoluble calcium carbonate.

The tallow is at first boiled with a weak soda-ley,[*] because the soap which is formed is insoluble in a strong alkaline solution, and would enclose and protect a quantity of undecomposed tallow; in proportion as the saponification proceeds, stronger leys are added, until the whole of the grease has disappeared. In order to separate the soap which is dissolved, advantage is taken of the insolubility of soap in solution of salt; a quantity of common salt being thrown into the boiler, the soap rises to the surface, when the *spent ley* is drawn off from below, and the soap transferred to iron moulds that it may harden sufficiently to be cut up into bars.

In order to understand the chemistry of this process, it is necessary to know that tallow contains two fatty substances, one of which, *stearin*[†] ($C_{57}H_{110}O_6$), is solid, and the other, *olein* ($C_{57}H_{104}O_6$), liquid, the quantity of stearin being about thrice that of olein.

When these fats are acted upon by soda, they undergo decomposition, furnishing stearic and oleic acids, which combine with the soda to form soap, whilst a peculiar sweet substance, termed *glycerin*, passes into solution; the nature of the decomposition in each case will be understood from the following equations—

$$\underset{\text{Stearin}}{C_3H_5.(C_{18}H_{35}O)_3.O_3} + 3NaHO = \underset{\text{Sodium stearate}}{3Na(C_{18}H_{35}O)O} + \underset{\text{Glycerin;}}{C_3H_8O_3}$$

$$\underset{\text{Olein}}{C_3H_5.(C_{18}H_{33}O)_3.O_3} + 3NaHO = \underset{\text{Sodium oleate}}{3Na(C_{18}H_{33}O)O} + \underset{\text{Glycerin;}}{C_3H_8O_3}$$

so that the soap obtained by boiling tallow with soda is a mixture of the sodium stearate with about a third of its weight of sodium oleate and 20 to 30 per cent. of water.

Palm oil is composed chiefly of *palmitin* ($C_{51}H_{98}O_6$), a solid fat which is resolved, by boiling with soda, into sodium palmitate (palm oil soap) and glycerin; $\underset{\text{Palmitin.}}{C_3H_5.(C_{16}H_{31}O)_3O_3} + 3NaHO = \underset{\text{Sodium palmitate.}}{3Na(C_{16}H_{31}O)O} + \underset{\text{Glycerin.}}{C_3H_8O_3}$

In the fish oils the predominant constituent is olein, so that when boiled with potassium hydrate, they yield potassium oleate ($KC_{18}H_{33}O_2$), which composes the chief part of *soft soap*.

Castile soap is made from olive oil, which contains olein and a solid fat known as *margarin*. The latter appears to be really composed of palmitin and stearin, so that the Castile soap is a mixture of oleate, palmitate, and stearate of sodium.

The peculiar appearance of *mottled soap* is caused by the irregular distribution of a compound of the fatty acid with oxide of iron, which arranges itself in veins throughout the mass. If the soap contained too much water, so as to render it very fluid when transferred to the moulds, this iron compound would settle down to the bottom, leaving the soap clear, so that the mottled appearance is often regarded as an indication that the soap does not contain an undue proportion of water; it is imitated, however, by stirring into the pasty soap some ferrous sulphate and a little impure ley containing sodium sulphide, so as to produce the dark sulphide of iron by double decomposition.[‡]

In the manufacture of *yellow soap*, in addition to tallow and palm oil, a considerable proportion of common rosin (see p. 483) is added to the soap shortly before it is finished. *Soft soap* is not separated from the water by salt like hard soap, but is evaporated to the required consistency. Transparent soaps are obtained by drying hard soap, dissolving it in hot spirit of wine, and pouring the strong solution into moulds after the greater part of the spirit has been distilled off. *Silicated soap* is a mixture of soap with silicate of soda. *Glycerin soap* is prepared by heating the fat with alkali and a little water to about 400° F. for two or three hours, and running the mass at once into moulds. It is, of course, a mixture of soap and glycerin.

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[*] Soap is now sometimes made by the action of the sodium carbonate upon the fat, thus saving the expense of caustifying (Morfit's process).

[†] Στέαρ, *tallow*.

[‡] A soap which contains much more than 30 per cent. of water is said not to admit of mottling.

The proportion of water in soaps is very variable, some specimens containing between 70 and 80 per cent. The smallest proportion is about 30 per cent.

The theory of saponification, stated above, has received the strongest confirmation within the last few years, by the synthetic production of the fats from glycerin and the fatty acids formed in their saponification.

CANDLES.

577. Since tallow fuses at about 100° F., and stearic acid not below 159°, it is evident that, independently of other considerations, the latter would be better adapted for the manufacture of candles, for such candles would never soften at the ordinary atmospheric temperature in any climate, and would have much less tendency to *gutter* in consequence of the excessive fusion of the fuel around the base of the wick. The gases furnished by the destructive distillation of stearic acid in the wick of the candle burn with a brighter flame than those produced from tallow. Accordingly, the manufacture of stearin (or more correctly, stearic acid) candles * has now become a very important and instructive branch of industry.

The original method of separating the stearic acid from tallow on the large scale consisted in mixing melted tallow with lime and water, and heating the mixture for some time to 212° by passing steam through it.

The tallow was thus converted into the insoluble stearate and oleate of calcium, which was drained from the solution containing the glycerin, and decomposed by sulphuric acid. The mixture of stearic and oleic acids thus obtained was cast into thin slabs, which were packed between pieces of cocoa-nut matting, and well squeezed in a hydraulic press, which forced out the oleic acid, leaving the stearic and palmitic acids in a fit state for the manufacture of candles.

The separation of the solid fatty acids from tallow and other fats may also be effected by the action of sulphuric acid, a process extensively applied in this country to palm and cocoa-nut oils. These fats are mixed in copper boilers with about one-sixth of their weight of concentrated sulphuric acid, and heated by steam to about 350° F. for some hours, when part of the glycerin is converted into sulphoglyceric acid ($C_3H_8O_3.SO_3$), and the remainder is decomposed by the sulphuric acid, carbonic and sulphurous acid gases being disengaged, whilst a dark-coloured mixture of palmitic, stearic, and oleic acid is left. A part of the oleic acid becomes converted in this process into *elaidic acid*, which has the same composition, but differs from oleic acid in fusing at about 113° F., so that the amount of solid acid obtained by this process is much increased. This mixture is well washed from the adhering sulphuric and sulphoglyceric acids, and transferred to a copper still into which a current of steam is passed, which has been raised to about 600° F. by passing through hot iron pipes. These fatty acids could not be distilled alone without decomposition, but under the influence of a current of steam they pass over readily enough, leaving a black pitchy residue in the retort, which is employed in making black sealing-wax, and for other useful purposes.

The distilled fatty acids are broken up and pressed between cocoa-nut matting to remove the oleic acid.

One great advantage of this process, which is commonly, though incorrectly, styled the *saponification by sulphuric acid*, is its allowing the conversion of the worst kinds of refuse fat into a form fit for the manufacture of candles; thus, the fat extracted from bones in the manufacture of glue, and that removed from wool in the scouring process, may be turned to profitable account.

It will be remarked that in this process the palmitic, stearic, and oleic acids are formed from the palmitin, stearin, and olein existing in the fats, by the assimilation of the elements of water and the subsequent separation of glycerin, just as in the ordinary process of saponification by means of alkalies.

Strictly speaking, the action appears to consist of two stages; for when concentrated sulphuric acid is allowed to act upon the natural fats in the cold, it combines with each of their ingredients, forming the acids known as sulphostearic, sulphopalmitic, sulpholeic, and sulphoglyceric, which are soluble in water, though not (with the exception of the last) in water containing sulphuric acid.

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* *Composite candles* are made of a mixture of stearic and palmitic acids.

The second stage consists in the decomposition of the sulpho-fatty acids by the high temperature in contact with steam, the sulphoglyceric acid having been in great measure decomposed into secondary products before the distillation is commenced.

Within the last few years, the extraction of the solid acids from the natural fats has been effected by a process known as *saponification by steam*, which allows the glycerin also to be obtained in a pure state. It is only necessary to subject the fat, in a distillatory apparatus, to the action of steam, at a temperature of about 600° F., to cause both the fatty acids and the glycerin to distil over; the former may be separated as usual into solid and liquid portions by pressure, whilst the glycerin, which is obtained in aqueous solution below the layer of fatty acids, is concentrated by evaporation, and sent into commerce as a very sweet colourless viscid liquid. The saponification of palmitin, for instance, by steam, would be represented by the equation—

$$\underset{\text{Palmitin.}}{C_3H_5.(C_{16}H_{31}O_2)_3} + 3H_2O = \underset{\text{Palmitic acid.}}{3(H.C_{16}H_{31}O_2)} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

STARCH.

578. Starch is manufactured chiefly from potatoes, wheat, and rice, the solid portion of which consists chiefly of starch, as appears in the following result of analysis:—

	Potatoes.	Wheat.	Rice.
Starch	20.2	60.8	83.0
Water	75.9	12.1	5.0
Gluten	...	10.5	6.0
Albumen	2.3	2.0	...
Dextrin and sugar	...	10.5	1.0
Woody fibre	0.4	1.5	4.8
Oily matter	0.2	1.1	0.1
Mineral matter	1.0	1.5	0.1
	100.0	100.0	100.0

In order to extract the starch, the potatoes are rasped to a pulp, which is washed upon a sieve, under a stream of water, as long as the latter is rendered milky by the starch suspended in it, the woody fibre being left behind upon the sieve. The milky liquid is allowed to settle, and the clear water drawn off; the deposited starch is then stirred up with fresh water, and again allowed to subside, this process being repeated as long as the water is coloured, after which the starch is mixed up with a small quantity of water, and passed through a fine sieve to separate mechanically mixed impurities; it is finally drained and dried, first in a current of air, and afterwards by a gentle heat.

Starch cannot be extracted from wheat so easily as from potatoes, on account of the much larger proportion of other solid matters from which it must be separated.

To extract the starch, the coarsely ground wheat is moistened with water, and allowed to putrefy, as it easily does, in consequence of the alterable character of the gluten (which contains carbon, hydrogen, nitrogen, oxygen, and sulphur); the putrefying gluten excites fermentation in the sugar and part of the starch, producing acetic and lactic acids. These acids are capable of dissolving the remainder of the gluten, which may then be washed away by water, the subsequent processes being similar to those employed in the extraction of potato starch.

A far more economical and scientific method of extracting the starch consists in dissolving the gluten by means of a weak alkaline solution, which leaves the starch untouched. This process is especially applied in the manufacture of starch from rice (p. 651).

Arrowroot is the starch extracted from the root of the *Maranta arundinacea*, and of some other tropical plants.

In the preparation of tapioca and sago, the starch is dried at a temperature above 140° F., so that it loses its ordinary farinaceous appearance and becomes semi-transparent.

Sago is manufactured from the pith of certain species of palm, natives of the East Indian islands. The tree is split so as to expose the pith, which is mixed with water, and the starch, having been separated from the woody fibre in the usual manner, is pressed through a perforated metallic plate, which moulds it into small cylinders; these are placed in a revolving vessel and broken into rough spherical grains, which are steamed upon a sieve, and dried.

Tapioca is obtained from the roots of the *Jatropha manihot*, a native of America. The roots are peeled and subjected to pressure, which squeezes out a juice employed by the Indians to poison their arrows, and containing a deleterious substance which has been named *jatrophine*. When the juice is allowed to stand, it deposits starch, which is well washed, pressed through a colander, and dried at 212° F.

Oswego, or corn-flour, is the flour of Indian corn deprived of gluten by treatment with a weak solution of soda.

579. Malting.—The tendency of starch to combine with the elements of water and pass into glucose (p. 647) is of immense importance in the chemistry of vegetation, as well as in that of food. It is, indeed, the chief chemical change concerned in the development of living from inanimate matter, being one of the first processes involved in the germination of a seed—the first step in the production of vegetables, which must precede the animals whose food they compose.

The components of all seeds are similar to those of wheat, which have been enumerated above; and if they be perfectly dried immediately after their removal from the parent plant, they may be preserved for a great length of time unchanged, and without losing the power of germinating under favourable circumstances. The essential conditions of germination are the presence of air and moisture, and a certain temperature, which varies with the nature of the seed. These conditions being fulfilled, the seed absorbs oxygen from the air, and evolves carbonic acid gas, produced by the combination of the oxygen with the carbon of one or more of the most alterable constituents of the seed, such as the vegetable albumen or the gluten. This process of oxidation is attended with evolution of heat, which serves to maintain the seed at the degree of warmth most favourable to germination. The component particles of the albumen or gluten, having been set in motion by the action of the atmospheric oxygen, induce a movement or chemical change in the starch with which they are in contact, causing it to pass into dextrin and glucose, which, unlike the starch, being perfectly soluble in water, are capable of affording to the developing shoot the carbon, hydrogen, and oxygen which it requires for the increase of its frame. The production of glucose and of dextrin in germination is well illustrated by the sweet gummy character of the bread made from *sprouted* wheat, and is turned to practical account in the process of malting.

During the germination of all seeds there is formed, apparently by the oxidation of one of the more alterable constituents, a peculiar substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained from any other source, and is characterised by its remarkable property of inducing the conversion of starch into dextrin and grape-sugar. This substance has been termed *diastase* (*διάστασις, dissension; metaph. fermentation*), but has never yet been obtained in a state of sufficient purity to enable its formula to be satisfactorily determined It may be extracted, however, from malt, by grinding it and mixing it with half its weight of warm water, which dissolves the diastase; the solution squeezed out of the malt is heated to about 170° F., filtered from any coagulated albumen, and mixed with absolute alcohol, which precipitates the diastase in white flakes. One part of diastase dissolved in water is capable of inducing the conversion of 2000 parts of starch into dextrin and grape-sugar, the diastase itself being exhausted in the process. A temperature of about 150° F. is most favourable to the action of diastase, which may be arrested entirely by raising the liquid to the boiling point.

The great importance of diastase in the arts of the brewer and distiller is at once apparent. In the process of *malting* barley, the grain is soaked in water, and afterwards spread out in thin layers upon the floor of a dark room (thus imitating the natural condition under which the seed germinates), which is maintained as nearly as possible at a constant and moderate temperature (between 55° and 62° F.); spring and autumn are, therefore, more favourable to malting than summer and winter. It soon evolves heat, and the grains begin to swell; in the course of twenty-four hours the germination commences, and the *radicle* makes its first appearance as a whitish protuberance; the grain is turned two or three times a day, in order to equalise the temperature. In about a fortnight the radicle has grown to about half an inch, by which time a sufficient quantity of diastase has been formed. In order to prevent the germination from proceeding further, the grain is killed by drying it at a temperature of 90° F. on perforated metallic plates, where it is afterwards heated to about 140° F., so as to render it brittle, after which it is sifted in order to separate the radicle, which is now easily broken off. This radicle is found to contain as much as $\frac{1}{9}$th of the total quantity of the nitrogen present in the barley, so that the *malt dust*, as the siftings are called, forms a valuable manure.

One hundred parts of barley generally yield about 80 parts of malt, but a part of the loss is due to water present in the barley, so that 100 parts of dry barley yield 90 parts of malt and 4 parts of malt dust, the difference, viz., 6 parts, representing the weight of the carbon converted into carbonic acid gas, of the hydrogen (if any) converted into water during the germination, and of soluble matters removed from the barley in steeping. Malt contains about $\frac{1}{500}$th of its weight of diastase, far more than enough to ensure the conversion of the whole of its starch into sugar.

The following table illustrates the change in composition suffered by barley during the process of malting, leaving the moisture out of consideration :—

	Barley.	After Steeping.	14½ Days on Floor.	Malt after Sifting.	Malt Dust.
Sugar	2.56	1.56	12.14	11.01	11.35
Starch Dextrin	80.42	81.12	70.09	72.03	43.68
Woody fibre	4.69	5.22	5.03	4.84	9.67
Albuminous matter	9.83	9.83	10.39	9.95	26.90
Mineral matter	2.50	2.27	2.35	2.17	8.40
	100.00	100.00	100.00	100.00	100.00

BREWING.

580. In order to prepare beer, the brewer *mashes* the ground malt with water at about 180° F., for some hours, when the diastase induces the conversion, into dextrin and sugar, of the greatest part of the starch which has not been so changed during the germination, and the *wort* is ready to be drawn off for conversion into beer. The undissolved portion of the malt, or *brewers' grains*, still contains a considerable quantity of starch and nitrogenised matter, and is employed for feeding pigs.

That malt contains far more diastase than is necessary to convert its starch into sugar, is shown by adding a little infusion of malt to the viscid solution of starch, and maintaining it at about 150° F. for a few hours, when the mixture will have become far more fluid, and will no longer be coloured blue by solution of iodine. In distilleries, advantage is taken of the excess of diastase in malt, by adding three or four parts of unmalted grain to it, when the whole of the starch in this latter is also converted into dextrin and sugar, and the labour and expense of malting it are avoided.

The wort obtained by infusing malt in water contains not only glucose, dextrin, and diastase, but a considerable quantity of nitrogenised matter formed from the gluten (or albuminous matter) of the barley. Before subjecting it to fermentation, it is boiled with a quantity of hops, usually amounting to about $\frac{1}{40}$th of the weight of the malt employed, which is found to prevent, in great measure, the tendency of the beer to become sour in consequence of the conversion of the alcohol into acetic acid.

The *hop* contains about 10 per cent. of an aromatic yellow powder, called *lupulin*, which appears to be the active portion, and which contains a volatile oil of peculiar odour, together with a very bitter substance.

The hopped wort is run off into a vat, where it is allowed to deposit the undissolved portion of the hops, and the clear liquor is drawn off into shallow coolers, where its temperature is lowered as rapidly as possible to about 60° F., the cooling being usually hastened by cold water circulating through pipes which traverse the coolers. If the wort be cooled too slowly, the nitrogenised matter which it contains undergoes an alteration by the action of the air, in consequence of which the beer is very liable to become acid.

The wort is now transferred to the *fermenting tun*, where it is made to ferment by the addition of yeast, usually in the proportion of $\frac{1}{100}$th of its volume.

Yeast is a minute fungoid vegetable, which grows in solutions containing sugar, together with some nitrogenised substance (*e.g.*, a salt of ammonium), and the salts (phosphates of potassium, sodium, calcium, and magnesium), which are essential constituents of its cells. If a little white of egg, cheese, or a piece of flesh (all of which contain carbon, hydrogen, nitrogen, oxygen, and phosphates) be placed in a solution of sugar, and allowed to undergo decomposition, a grey scum forms upon the liquid, which is seen under the microscope to consist of irregularly oval cells, the growth of which may be watched under the microscope in a little of the liquid from which they were obtained, when they will be found to multiply rapidly by the production of new cells on all sides of them (fig. 288). The same cells will be developed very rapidly in the sweet wort of malt, allowed to undergo decomposition between 60° and 70° F.

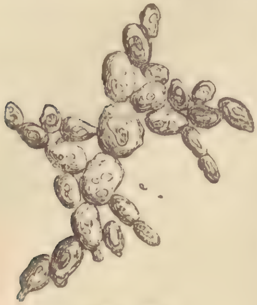

Fig. 288.

These cells contain a substance somewhat resembling albumen, enclosed in a thin membrane, the composition of which is similar to that of cellulose. They also contain a peculiar nitrogenised body resembling diastase, and capable of inducing the conversion of cane-sugar ($C_{12}H_{22}O_{11}$) into glucose ($C_6H_{12}O_6$). Accordingly, when yeast is added to a solution of cane-sugar, the liquid is found to increase in specific gravity (a solution of cane-sugar having a lower density than one containing an equivalent quantity of glucose) previously to the commencement of fermentation, and the application of tests readily proves the presence of glucose in the solution.

The glucose then undergoes the decomposition known as *alcoholic fermentation*, which results in the production of alcohol, carbonic acid, lactic acid, succinic acid, glycerin, and a peculiar brown soluble matter, together with other substances, the true nature of which is yet undetermined. The fermentation is attended with a considerable elevation of temperature.

Taking into consideration only the alcohol and carbonic acid gas, which are the chief products, their formation from grape-sugar may be represented by the equation $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$.

During the fermentation, the yeast cells are gradually broken up, so that a given quantity of yeast is capable of fermenting only a limited quantity of sugar. On an average, a quantity of yeast containing between two and three parts of solid matter is required to complete the fermentation of 100 parts of sugar. The solution remaining after the fermentation is found to contain salts of ammonium, which have been formed at the expense of the nitrogen of the yeast.

If the liquid in which the yeast excites fermentation contains nitrogenised matters and phosphates, the yeast-plant grows, and its quantity increases; thus, in the sweet wort from malt, the yeast is nourished by the altered gluten and by the phosphates, so that it increases to six or eight times its original weight.

If yeast be heated to the boiling point of water, the plant is killed, as might be expected, and loses its power of inducing alcoholic fermentation; but it may be dried at a low temperature, or by pressure, without losing its fermenting power, and *dried yeast* is an article of commerce. German dried yeast is produced in the fermentation of rye for making Hollands.

Yeast will not cause fermentation in a solution containing more than one-fourth of its weight of sugar, and the fermentation is arrested when the alcohol amounts to one-fifth of the weight of the liquid, so that the strength of fermented liquors could never exceed 20 per cent. of alcohol. The fermentation is also arrested by the mineral acids, and by many of the substances to which antiseptic properties are commonly attributed, such as common salt, kreasote, corrosive sublimate, sulphurous acid, turpentine, &c.

In the fermentation of beer, the yeast is carried up to the surface by the effervescence due to the escape of the carbonic acid gas, and is eventually removed, in order to be employed for the fermentation of fresh quantities of wort. When the fermentation has proceeded to the required extent, the beer is stored for consumption.

It will be seen that the chief constituents of beer are the alcohol, the nitrogenised substance derived from the albuminous matter of the barley, and not consumed in the growth of the yeast, the unaltered glucose and dextrin, the brown or yellow colouring matter formed during the fermentation, the essential oil and bitter principle of the hop.

Beer also contains acetic acid (formed by the oxidation of the alcohol, page 510), free carbonic acid, which gives its sparkling character, together with the lactic and succinic acids and glycerin, formed as secondary products of the fermentation, and ammoniacal salts derived from the yeast. The soluble mineral substances from the barley are also present, *minus* the phosphates abstracted by the yeast.

The proportions of the constituents, of course, vary greatly, as will be seen from the following examples:—

Percentage.	Allsopp's Ale.	Bass's Ale.	Strong Ale.	Whitbread's Porter.	Whitbread's Stout.
Alcohol . . .	6.00	7.00	8.65	4.20	6.00
Acetic acid . .	0.20	0.18	0.12	0.19	0.18
Sugar and other solid matters	5.00	4.80	6.60	5.40	6.38

The dark colour of porter and stout is caused by the addition of a quantity of *high-dried malt* which has been exposed to so high a temperature in the kiln as to convert a portion of its sugar into a dark brown soluble substance called caramel. The peculiar aroma of beer is probably due to the presence of acetic ether, produced during the fermentation.

In some cases, when the operation of brewing has been badly conducted, the beer becomes *ropy* or undergoes the *viscous fermentation*. In this case the glucose suffers a peculiar transformation, resulting in the production of a mucilaginous substance resembling gum in its composition. This change may be induced by yeast which has been boiled, or by water in which flour or rice has been steeped. White wine occasionally becomes ropy from a similar cause, but red wines are not liable to this change, apparently because the tannin which they contain has precipitated in an insoluble form the ferment which induces it. During this viscous fermentation a part of the glucose is often converted into mannite ($C_6H_{14}O_6$).

WINE AND SPIRITS.

580*a*. Wine is essentially composed of 8 or 10 parts of alcohol, with 85 or 90 of water, together with minute quantities of certain fragrant ethers, of colouring matter, of potassium bitartrate, and of the mineral substances derived from the grape-juice. Glycerin and succinic acid have also been found in wines, and appear to be constant secondary products of the alcoholic fermentation.

Those wines in which the whole of the sugar has been fermented are known as *dry* wines; whilst *fruity* wines still retain a considerable quantity of sugar.

The preparation of wines differs from that of beer in the circumstance that no addition of ferment is necessary, the fermentation being spontaneous. Grape juice contains, in addition to grape-sugar, vegetable albumen, potassium tartrate, and the usual mineral salts found in vegetable juices. The husks, seeds, and stalks of the grape contain a considerable quantity of tannin, together with certain blue, red, and yellow colouring matters.

When the expressed juice remains for a short time in contact with the air, the germs or spores of yeast (p. 704) which float in the air, are deposited on the surface of the juice, at the expense of which they begin to grow, exciting the vinous fermentation in the sugar, and a scum of yeast is formed upon the surface. If this fermentation takes place in contact with the husks of the dark grapes, the alcohol dissolves the colouring matter, and a red wine results; whilst for the production of white wines, the husks, &c., are separated previously to the fermentation, and the juice is exposed as little as possible to the air.

White wines are rather liable to become *ropy* from viscous fermentation, but this is prevented by the addition of a small quantity of tannin, which precipitates the peculiar ferment. The tannin for this purpose is extracted from the husks and stalks of the grapes themselves.

Red wines, such as port and claret, are often very astringent from the tannin dissolved out of the husks, &c., during the fermentation. Port wine, when freshly bottled, still retains in solution a considerable quantity of acid potassium tartrate or bitartrate of potash ($KHC_4H_4O_6$), but after it has been kept some time, and become more strongly alcoholic, this salt is deposited, together with a quantity of the colouring matter, in the form of a crust upon the side of the bottle. Thus a dark *fruity* port becomes *tawny* and *dry* when kept for a sufficient length of time, the sugar having been converted into alcohol.

When the wine contains an excess of tartaric acid, it is customary to add to it some neutral potassium tartrate ($K_2C_4H_4O_6$), which precipitates the acid in the form of bitartrate.

The preparation of champagne is conducted with the greatest care. The juice or *must* is carefully separated from the *marc* or husks, and is often mixed with 1 per cent. of brandy before fermentation. After about two months the wine is drawn off into another cask, and clarified with isinglass dissolved in white wine, and added in the proportion of about half an ounce to 40 gallons. This combines with the tannin to form an insoluble precipitate, which carries with it any impurities floating in the wine. After another interval of two months, the wine is again drawn off, and a second clarification takes place; and in two months more the wine is drawn off into bottles containing a small quantity of pure sugar-candy dissolved in white wine. The bottles, having been securely corked and wired, are laid down upon their sides for eight or ten months, during which time the fermentation of the newly added sugar takes place, and the carbonic acid produced dissolves in the wine, whilst a quantity of yeast is separated. In order to render the wine perfectly clear, the bottle is left for about three weeks in such a position that the deposit may subside into the neck, against the cork, which is then unwired so that the pressure of the accumulated carbonic acid gas may force it out together with the deposit; the bottle having been rapidly filled up with white wine, is again corked, wired, covered with tin foil, and sent into the market. Pink champagne is prepared from the must which is squeezed out of the marc after it has ceased to run freely, and contains a little of the colouring matter of the husk. The colour is also sometimes imparted by adding a little tincture of litmus.

The proportion of alcohol in wines varies greatly, as will be seen from the following statement of the weight of alcohol in 100 parts of the wine :—

Port . .	15 to 17	Claret . .	8 to 9
Sherry . .	14 to 16	Rudesheimer . .	7 to 8.5
Champagne . .	11.5		

Sherry contains from 1 to 5 per cent. of sugar, port from 3 to 7 per cent., and Tokay 17 per cent. ; in the last case, the sugar is increased by adding some of the must, concentrated by evaporation, to the wine previously to bottling.

The *bouquet* or fragrance of wine is due to the presence of certain fragrant ethers (*ethereal salts*) especially of œnanthic, pelargonic, and acetic ether, formed during the fermentation or during the subsequent storing of the wine. It is to the increased quantity of such fragrant ether that the superior bouquet of many old wines is due.

Distilled spirits.—The varieties of ardent spirits are obtained from fermented liquids by distillation, so that they consist essentially of alcohol more or less diluted with water, and flavoured either with some of the volatile products of the fermentation, or with some essential oil added for the purpose.

Brandy is distilled from wine, and coloured to the required extent with burnt sugar (caramel). Its flavour is due chiefly to the presence of œnanthic ether derived from the wine. The colour of genuine pale brandy is due to its having remained so long in the cask as to have dissolved a portion of brown colouring matter from the wood, and is therefore an indication of its age. Hence arose the custom of adding caramel, and sometimes infusion of tea, to impart the colour and astringency due to the tannin dissolved from the wood by old brandy.

Whisky is distilled from fermented malt, which has been dried over a peat fire, to which the characteristic smoky flavour is due.

Gin is also prepared from fermented malt or other grain, and is flavoured with the essential oil of juniper, derived from juniper berries added during the distillation.

Rum is distilled from fermented molasses, and appears to owe its flavour to the presence of butyric ether, or of some similar compound.

Arrack is the spirit obtained from fermented rice.

Kirschwasser and *maraschino* are distilled from cherries and their stones, which have been crushed and fermented.

Some varieties of British brandy and whisky are distilled from fermented potatoes, or from a mixture of potatoes and grain, when there distils over, together with ordinary alcohol, especially towards the end of the distillation, another spirit belonging to the same class, but distinguished from alcohol by its nauseous and irritating odour. This substance, which is known as *potato-spirit*, *amylic alcohol*, or *fousel oil* ($C_5H_{12}O$), also occurs, though in very minute quantity, in genuine wine brandy. The manufacturers of spirit from grain and potatoes remove a considerable part of this disagreeable and unwholesome substance by leaving the spirit for some time in contact with wood-charcoal.

BREAD.

581. The chemistry of fermentation is intimately connected with the ordinary process of bread-making. It will be remembered that wheaten flour (p. 701) consists, essentially, of starch and gluten, with a little dextrin and sugar. On mixing the flour with a little water, it yields a *dough*, the tenacity of which is due to the gluten present in the flour. If this dough be tied up in a piece of fine muslin, and kneaded under a stream of water, the starch will be suspended in the water, and will pass through the muslin, whilst the gluten will remain as a very tough elastic mass, which speedily putrefies if exposed to the air in a moist state, and dries up to a brittle horny mass at the temperature of boiling water.

On analysis, gluten is found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which may be represented by the empirical formula $C_{24}H_{40}N_6O_7$, though it cannot be regarded as a single independent substance, but as a mixture of three substances very closely allied in composition.

When gluten is boiled with alcohol, one portion refuses to dissolve, and has been named *vegetable fibrin*, from its resemblance to the substance forming the muscles of animals. When the solution in alcohol is allowed to cool, it deposits a white flocculent matter, very similar to the *casein* which composes the curd of milk. On adding water to the cold alcoholic solution, a third substance (*glutin*) is separated, which much resembles the albumen found so abundantly in the blood.

The presence in gluten of three substances, similar to the three principal components of the animal body, leads us to form a high opinion of its value as a nutritive compound. But gluten itself, separated from the flour by the process above described, would be found very difficult of digestion, on account of its resistance to the solvent action of the fluids in the stomach; indeed, the dough composed of flour and water is proverbially indigestible, even when baked. In order to render it fit for food, it must be rendered spongy or porous, so as to expose a larger surface to the action of the digestive fluids of the body; the most direct method of effecting this is the one adopted in the manufacture of the *aerated bread*, and consists in mixing the flour with water which has been highly charged, under pressure, with carbonic acid gas; the mixing having been effected in a strong closed iron vessel, an aperture in the lower part of this is opened, when the pressure of the accumulated gas forces the dough out into the air, and the gas which has been imprisoned in the dough expands, conferring great porosity and sponginess upon the mass in its attempt to escape. In another process for preparing *unfermented bread*, the flour is mixed with a little bicarbonate of soda, and is then made into a dough with water acidulated with hydrochloric acid; the latter decomposing the bicarbonate of soda, liberates carbonic acid gas, which renders the bread porous. The sodium chloride formed at the same time remains in the bread. In the preparation of cakes and pastry, the same object is sometimes attained by adding carbonate of ammonia to the dough; when heat is applied in the baking, the salt is converted into vapour which distends the dough.

In the common process of bread making, however, the carbonic acid gas destined to confer sponginess upon the dough is evolved by the fermentation of the sugar contained in the flour; the latter having been kneaded with the proper proportion (usually about half its weight) of water, a little yeast and salt are added, and the mixture is allowed to stand at a temperature of about 70° F. for some hours. The dough swells or *rises* considerably in consequence of the escape of carbonic acid gas, the sugar being decomposed into that gas and alcohol, as in ordinary fermentation. The spongy dough is then baked in an oven, heated to about 500° F., when a portion of the water and the whole of the alcohol are expelled, the carbonic acid gas being also much expanded by the heat, and the porosity of the bread increased. The granules of starch are much altered by the heat, and become far more digestible. Although the temperature of the inside of the loaf does not exceed 212° F., the outer portion becomes torrefied or scorched into crust.

Occasionally, instead of yeast, *leaven* is employed, in order to ferment the sugar, leaven being dough which has been left in a warm place until decomposition has commenced.

The passage of new into stale bread does not depend, as was formerly supposed, upon the drying of the bread consequent upon its exposure to air, but is a true molecular transformation which takes place equally well in an air-tight vessel, and without any loss of weight. It is well known that when a thick slice of stale bread is toasted, which *dries* it still further, the crumb again becomes soft and spongy as in new bread; and if a stale loaf be again placed in the oven, it is entirely reconverted into new bread.

Wheaten flour is particularly well fitted for the preparation of bread on account of the great tenacity of its gluten. Next to wheat in this respect stands rye, whilst the other cereals contain a gluten so deficient in tenacity that it is impossible to convert them into good bread.

Barley bread is close and heavy, since its nitrogenised matter is chiefly present in the form of albumen, which does not vesiculate like gluten during the fermentation. Even in wheaten flour the tenacity of the gluten is liable to variation, and in order to obtain good bread from a flour the gluten of which is inferior in this respect, it is customary to employ a minute proportion of alum. This addition being considered unwholesome by some persons, it would be better to substitute lime-water, which has been found by Liebig to have a similar effect. Sulphate of copper improves in a very striking manner the quality of the bread prepared from inferior flour, but this salt is far more objectionable than alum.

TEA, COFFEE, ETC.

582. A very remarkable instance of the application of chemistry to explain the use of widely different articles of diet by different nations, with a view to the production of certain analogous effects upon the system, is seen in the case of coffee, tea, Paraguay tea, and the *kola nut* (of Central Africa), which are very dissimilar in their sensible properties, and afford little or no gratification to the palate, owing what attractions they possess chiefly to the presence, in each, of one and the same active principle or alkaloid, which has a special effect upon the animal economy. This alkaloid is known as caffein or thein, and is associated in the three articles of diet mentioned above, with various substances, which give rise to their diversity in flavour.

The raw coffee-berry presents, on the average, the following composition:—

100 *parts of Raw Coffee contain—*

Woody fibre	34.0
Water	12.0
Fat	12.0
Cane-sugar and gum	15.5
Legumin, or some allied substance	13.0
Caffeine	1.5
Caffeic acid	4.0
Mineral substances	7.0

When the raw berry is treated with hot water, the infusion, which contains the sugar and gum, the legumin, caffeine, and *caffeic acid* ($C_9H_8O_4$), has none of the peculiar fragrance which distinguishes the ordinary beverage, and is due to an aromatic volatile oily substance termed *caffeol* ($C_8H_{10}O_2$) formed during the roasting to which the berry is subjected before use. This volatile oil, which is present in very minute quantity, is produced from one of the soluble constituents of the berry (probably from the caffeic acid), for if the infusion of raw coffee be evaporated to dryness, the residue, when heated, acquires the characteristic odour of roasted coffee.

Acetic and palmitic acids are also found among the products of coffee-roasting.

The roasting is effected in ovens at a temperature rather below 400° F., when the berry swells greatly, and loses about ¼th of its weight, becoming brittle, and easily ground to powder. It also becomes very much darker in colour, from the conversion of the greater part of its sugar into caramel (p. 644), which imparts the dark brown colour to the infusion of coffee. If the roasting be carried too far, a very disagreeable flavour is imparted to the coffee by the action of heat upon the legumin and other nitrogenised substances contained in the berry.

From 100 parts of the roasted coffee, boiling water extracts about 20 parts, consisting of caffeine, caffeic acid, caramel, legumin, a little suspended fatty matter, fragrant volatile oil (caffeone), and salts of potassium (especially the phosphate). The undissolved portion of the coffee contains, beside the woody fibre, a considerable quantity of nitrogenised (and nutritious) matter, and hence the custom, in some countries, of taking this residue together with the infusion.

The constituents of the leaves of the tea-plant (*Thea sinensis*) exhibit a general similarity to those of the coffee-berry. In the fresh leaf we find, in addition to the woody fibre, a large quantity of a substance containing nitrogen, similar to legumin, an astringent acid similar to tannic acid, a small quantity of caffeine, and some mineral constituents.

The aroma of tea does not belong to the fresh leaf, but is produced, like that of coffee, during the process of drying by heat, which develops a small quantity of a peculiar volatile oil, having powerful stimulating properties. The freshly dried leaf is comparatively so rich in this oil that it is not deemed advisable to use it until it has been kept for some time.

Green and black tea are the produce of the same plant, the difference being caused by the mode of preparation. For green tea the leaves are dried over a fire as soon as they are gathered, whilst those intended for black tea are allowed to remain exposed to the air in heaps for several hours, and are then rolled with the hands and partially dried over a fire, these processes being repeated three or four times to develop the desired flavour. The black colour appears to be due to the action of the air upon the tannin present in the leaf.

Boiling water extracts about 30 parts of soluble matter from 100 of black tea, and 36 from 100 of green tea. The principal constituents of the infusion of tea are tannin, aromatic oil, of which green tea contains about 0.8 and black tea 0.6 per cent., and caffeine, the proportion of which, in the dried leaf, varies from 2.2 to 4.1 per cent., being present in larger quantity in green tea.

The spent leaves contain the greater part of the legumin and a considerable quantity of caffeine, which may be extracted by boiling them with water, and treating the decoction as at p. 600.

Cocoa and *chocolate* are prepared from the cacao-nut, which is the seed of *Theobroma cacao*, and is characterised by the presence of more than half of its weight (*minus* the husk) of a fatty substance known as *cacao-butter*, and consisting of olein and stearin, which does not become rancid like the natural fats generally. The cacao-nut also contains a large quantity of starch, a nitrogenised substance resembling gluten, together with gum, sugar, and *theobromine*, a feeble base very similar to caffeine, but having the composition $C_7H_8N_4O_2$.

The seeds are allowed to ferment in heaps for a short time, which improves their flavour, dried in the sun and roasted like coffee, which develops the peculiar aroma of cocoa. The roasted beans having been crushed and winnowed to separate the husks, are ground in warm mills, in which the fatty matter melts and unites with the ground beans to a paste, which is mixed with sugar and pressed into moulds. In the preparation of chocolate, vanilla and spices are also added.

From the composition of cocoa and chocolate it is seen that when consumed, as is usual, in the form of a paste, they would prove far more nutritious than mere infusions of tea and coffee.

ANIMAL CHEMISTRY.

583. Our acquaintance with the chemistry of the substances composing the bodies of animals is still very limited, although the attention of many accomplished investigators has been directed to this branch of the science. The reasons for this are to be found, firstly, in the susceptibility to change exhibited by animal substances, when removed from the influence of life; and secondly, in the absence, in such substances, of certain physical properties by which we might be enabled to separate them from other bodies with which they are associated, and to verify their purity when obtained in a separate state. Two of the most important of these properties are volatility and the tendency to crystallise. When a substance can suffer distillation without change, it will be remembered that its boiling-point affords a criterion of its purity; or if it be capable of crystallising, this may be taken advantage of in separating it from other substances which

crystallise more or less easily than itself, and its purity may be ascertained from the absence of crystals of any other form than that belonging to the substance. But the greater number of the components of animal frames can neither be crystallised nor distilled, so that many of the analyses which have been made of such substances differ widely from each other, because the analyst could never be sure of the perfect purity of his material; and even when concordant results have been obtained as to the percentage composition of the substance, the formula deduced from it has been of so singular and exceptional a character as to cast very strong suspicion upon the purity of the substance.

Accordingly, the chemical formulæ of a great many animal substances are perfectly unintelligible, conveying not the least information as to the position in which the compound stands with respect to other substances, or the changes which it might undergo under given circumstances.

The extraordinary formulæ, for example, deduced from the ultimate analysis of *albumen*, $C_{72}H_{112}N_{18}SO_{22}$, and *casein*, $C_{144}H_{228}N_{36}O_{45}S$, cannot be referred to any known type, and refuse to be classed with other substances.

Animal chemistry is, for the above reasons, in a very backward condition, as compared with vegetable and mineral chemistry, though an observation of the progress of research affords us the consolation, that a steady advance is being made towards a generalisation of the facts which have been discovered, especially by analogical reasoning from those two other departments of the science.

584. MILK.—The chemistry of milk is well adapted to introduce the study of animal chemistry, because that liquid contains representatives of all the substances which make up the animal frame; and it is on this account that it occupies so high a position among articles of food.

Although, to the unaided eye, milk appears to be a perfectly homogeneous fluid, the microscope reveals the presence of innumerable globules floating in a transparent liquid, which is thus rendered opaque. If milk be very violently agitated for several hours, masses of an oily fat (butter, p. 697) are separated from it, and leave the liquid transparent. This fat was originally distributed throughout the milk, in minute globules enclosed in very thin membranes which were torn by the violent agitation, and the fatty globules then cohered into larger masses.

For the preparation of butter, it is usual to allow the milk to stand for some hours, when a layer of *cream* collects upon the surface, the proportion of which is very variable, but is generally about $\frac{1}{10}$th of the volume of the milk.* The *skimmed milk* retains about half of the fatty matter. This cream contains about 5 per cent. (by weight) of fat, 3 per cent. of casein, and water. When the cream is *churned*, the enclosing membranes of the fat globules are broken, and the fat unites into a semi-solid mass of butter, from which the butter-milk containing the casein may be separated. If this be not done effectually, the casein which is left in the butter, being a nitrogenised substance, will soon begin to decompose, and will induce a decomposition in the butter (p. 697), resulting in the formation of certain volatile acids, which impart to it a rancid and offensive taste and odour. To prevent this, salt is generally added to butter which has been less carefully prepared, in order to preserve the casein from decomposition. *Butter-milk* contains about one-fourth of the fatty matter of the milk.

Pure butter is essentially a mixture of margarin and olein with smaller quantities of other fats, such as butyrin, caprin, and caproin (p. 697).

Fresh milk is slightly alkaline to test-papers, but after a short time it acquires an acid reaction; and if it be then heated, it coagulates from the separation of the casein. This spontaneous acidification of milk is caused by the fermentation of the *sugar of milk*, which results in the production of *lactic acid*.

If milk be maintained at a temperature of about 90° F., the fermentation results in the production of alcohol and carbonic acid, for although milk-sugar is not fermented like ordinary sugar by contact with yeast, it appears, under the influence of the changing casein at a favourable temperature, to be converted first into grape-sugar (p. 647), and afterwards into alcohol and carbonic acid. The Tartars prepare an intoxicating liquid which they call *koumiss*, by the fermentation of milk.

When an acid is added to milk, the casein is separated in the form of curd, in consequence of the neutralisation of the soda which retains it dissolved in fresh milk, and this curd carries with it, mechanically, the fat globules of the milk, leaving a clear yellow *whey*.

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* The separation of cream is now effected, in large dairies, by means of a *centrifugal separator* making several thousand revolutions per minute.

In the preparation of *cheese*, the milk is coagulated by means of *rennet*, which is prepared from the lining membrane of a calf's stomach. This is left in contact with the warm milk for some hours, until the coagulation is completed. This action of rennet upon milk depends upon the presence of certain microscopic organisms. The curd is collected and pressed into cheeses, which are allowed to ripen in a cool place, where they are occasionally sprinkled with salt. The peculiar flavour which the cheese thus acquires is due to the decomposition of the casein, giving rise to the production of certain volatile acids, such as butyric, valerianic, and caproic, which have very powerful and characteristic odours. If this ripening be allowed to proceed very far, ammonia is developed by the putrefaction of the casein, and in some cases the ethers of the above-mentioned acids are produced, at the expense probably of a little sugar of milk left in the cheese, conferring the peculiar aroma perceptible in some varieties of it.

The different kinds of cheese are dependent upon the kind of milk used in their preparation, the richer cheeses being, of course, obtained from milk containing a large proportion of cream; such cheese fuses at a moderate heat, and makes good toasted cheese, whilst that which contains little butter never fuses completely, but dries and shrivels like leather. Double Gloucester and Stilton are made from a mixture of new milk and cream; Cheddar cheese is made from new milk alone. Cheshire and American cheeses, from milk robbed of about one-eighth of its cream. Dutch cheese and the *Skim Dick* of the midland counties, from skimmed milk.

The characteristic constituents of milk are the casein and milk-sugar, but the proportions in which these are present vary widely not only with the animal from which the milk is obtained, but with the food and condition of the animal. A general notion of their relative quantities, however, may be gathered from the following table, exhibiting the results of the analyses made by Boussingault:—

	Cow.	Ass.	Goat.	Woman.
Water . . .	87.4	90.5	82.0	88.4
Butter . . .	4.0	1.4	4.5	2.5
Milk-sugar . Soluble salts	5.0	6.4	4.5	4.8
Casein . Insoluble salts	3.6	1.7	9.0	3.8

The soluble salts present in milk include the phosphates and chlorides of potassium and sodium, whilst the insoluble salts are the phosphates of calcium, magnesium, and iron. All these salts are in great request for the nourishment of the animal frame.

The milk supplied to consumers living in towns is subject to considerable adulteration; but in most cases this is effected by simply removing the cream and diluting the skimmed milk with water, a fraud which is not easily detected, as might be supposed, by determining the specific gravity of the milk, for since milk is heavier than water (1·032 sp. gr.), and the fatty matter composing cream is lighter than water, a certain quantity of cream might be removed, and water added, without altering the specific gravity of the milk.

The simplest method of ascertaining the quality of the milk consists in setting it aside for twenty-four hours in a tall narrow tube (*lactometer* or *creamometer*) divided into 100 equal parts, and measuring the proportion of cream which separates, this averaging, in pure milk, from eleven to thirteen divisions. The measurement of the cream is effected in fifty minutes by using a *centrifugal separator*, in which the tube containing the milk is placed in a case attached to a centrifugal apparatus making 1200 revolutions per minute. By shaking milk with a little potash (to dissolve the membrane which envelopes the fat globules) and ether, the butter may be dissolved in the ether which rises to the surface, and if this be poured off and allowed to evaporate, the weight of the butter may be ascertained; or the milk may be evaporated by a steam heat, and the fat dissolved by treating the residue with ether. The amount of fat is sometimes found by taking the specific gravity of the ethereal solution, and referring to a table giving the corresponding quantity of fat. One thousand grains of milk should give, at least, 27 or 28 grains of butter. Since, however, the milk of the same cow gives very different quantities of cream at different times, it is difficult to state confidently that adulteration has been practised. The standard usually adopted by analysts is 25 grains of fat or butter and 90 grains of "solids not fat" in 1000 grains of milk.

585. Blood.—The blood from which the various organs of the body directly receive their nourishment is the most important, as well as the most complex, of the animal fluids. Its chemical examination is attended with much difficulty, on account of the rapidity with which it changes after removal from the body of the animal.

On examining freshly drawn blood under the microscope, it is observed to present some resemblance to milk in its physical constitution, consisting of opaque flattened globules floating in a transparent liquid; the globules, in the case of blood, having a well-marked red colour.

In a few minutes after the blood has been drawn, it begins to assume a gelatinous appearance, and the semi-solid mass thus formed separates into a red solid portion or *clot*, which continues to shrink for ten or twelve hours, and a clear yellow liquid or *serum*. It might be supposed that this coagulation is due to the cooling of the blood, but it is found by experiment to take place even more rapidly when the temperature of the blood is raised one or two degrees after it has been drawn; and on the other hand, if it be artificially cooled, its coagulation is retarded. Indeed, the reason for this remarkable behaviour of the blood is not yet understood.

If the coagulum or clot of blood be cut into slices, tied in a cloth, and well washed in a stream of water, the latter runs off with a bright red colour, and a tough yellow filamentous substance is left upon the cloth; this substance is called *fibrin*, and its presence is the proximate cause of the coagulation of the blood, for if the fresh blood be well whipped with a bundle of twigs or glass rods, the fibrin will adhere to them in yellow strings, and the *defibrinated* blood will no longer coagulate on standing. If this blood, from which the fibrin has been extracted, be mixed with a large quantity of a saline solution (for example, 8 times its bulk of a saturated solution of sodium sulphate), and allowed to stand, the red globules subside to the bottom of the vessel.

These globules are minute bags of red fluid, enclosed in a very thin membrane or *cell-wall*, and if water were mixed with the defibrinated blood, since its specific gravity is lower than that of the fluid in the globules, it would pass through the membrane (by *endosmose*), and so swell the latter as to break it and disperse the contents through the liquid.

The red fluid contained in these blood globules consists of an aqueous solution, containing as its principal constituents a substance known as *globulin*, which very nearly resembles albumen, and the peculiar colouring matter of the blood, which is called *hæmatin*.

Beside these, the globules contain a little fatty matter and certain mineral constituents, especially the iron (which is associated in some unknown form with the colouring matter), the chlorides of sodium and potassium, and the phosphates of potassium, sodium, calcium, and magnesium.

Though the quantities of these constituents are not invariable, even in the same individual, the following numbers may be taken as representing the average composition of these globules:—

1000 *parts of Blood Globules contain—*

Water	688.00	Organic substances of unknown nature	2.60
Globulin	282.22	Mineral substances*	8.12
Hæmatin	16.75		
Fat	2.31		

The mineral substances consist of—

Potassium	3.328	Oxygen	0.667
Phosphoric oxide (P_2O_5)	1.134	Calcium phosphate	0.114
Sodium	1.052	Magnesium phosphate	0.073
Chlorine	1.686	Sulphuric oxide (SO_3)	0.066

The liquid in which the blood globules float is an alkaline solution containing albumen, fibrin, and saline matters in about the proportions here indicated.

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* Exclusive of the iron which is associated with the hæmatin.

1000 *parts of Liquor Sanguinis contain—*

Water	902.90	Organic substances of unknown nature	3.94
Albumen	78.84	Mineral substances	8.55
Fibrin	4.05		
Fat	1.72		

The Mineral substances consist of—

Sodium	3.341	Phosphoric oxide (P_2O_5)	0.191
Chlorine	3.644	Sulphuric oxide (SO_3)	0.115
Potassium	0.323	Calcium phosphate	0.311
Oxygen	0.403	Magnesium phosphate	0.222

The alkaline character of this liquid appears to be due to the presence of carbonate and phosphate of sodium.

586. Flesh.—The fibrin composing muscular flesh contains about three-fourths of its weight of water, a part of which is due to the blood contained in the vessels traversing it, and another part to the *juice of flesh*, which may be squeezed out of the chopped flesh. In this juice of flesh there are certain substances which appear to play a very important part in nutrition. The liquid is distinctly acid, which is remarkable when the alkaline character of the blood is considered, and contains phosphoric, lactic, and butyric acid, together with kreatine (p. 674) inosite (p. 649) and saline matters. By soaking minced flesh in cold water and well squeezing it in a cloth, a red fluid is obtained containing the juice of flesh mixed with a little blood.

The saline constituents of the juice of flesh are chiefly phosphates of potassium and magnesium, with a little chloride of sodium. It is worthy of notice that potassium is the predominant alkali-metal in the juice of flesh, whilst sodium predominates in the blood, especially in the serum.

According to Liebig, the acidity of the juice of flesh is chiefly due to the acid phosphate of potassium, KH_2PO_4, whilst the alkalinity of the blood is caused by sodium phosphate, Na_2HPO_4; and it has been suggested that the electric currents which have been traced in the muscular fibres are due to the mutual action between the acid juice of flesh and the alkaline blood, separated only by thin membranes from each other, and from the substance of the muscles and nerves.

The average composition of flesh may be represented as follows:—

Water	78
Fibrin, vessels, nerves, cells, &c.	17
Albumen	2.5
Other constituents of the juice of flesh	2.5
	100.0

Liebig's extract of meat is prepared by exhausting all the soluble matters from the flesh with cold water, separating the albumen by coagulation, and evaporating the liquid at a steam heat to a soft extract. It contains about half its weight of water, 40 per cent. of the organic constituents of the juice of flesh (albumen excepted), and 10 per cent. of saline matter.

Cooking of meat.—A knowledge of the composition of the juice of flesh explains the practice adopted in boiling meat, of immersing it at once in boiling water, instead of placing it in cold water, which is afterwards raised to the boiling-point. In the latter case, the water would soak into the meat, and remove the important nutritive matter contained in the juice; whilst, in the former, the albumen in the external layer of flesh is at once coagulated, and the water is prevented from penetrating to the interior. In making soup, of course, the opposite method should be followed, the meat being placed in cold water, the temperature of which is gradually raised, so that all the juice of flesh may be extracted and the muscular fibre and vessels alone left.

The object to be attained in the preparation of *beef-tea*, is the extraction of the whole of the soluble matters from the flesh, to effect which the meat should be minced as finely as possible, soaked for a short time in an equal weight of cold water, and slowly raised to the boiling point, at which it is maintained for a few minutes. The liquid strained from the residual fibrin contains all the constituents of the juice except the albumen, which has been coagulated.

When meat is roasted, the internal portions do not generally attain a sufficiently high temperature to coagulate the albumen of the juice, but the outside is heated far above 212° F.; so that the meat becomes impregnated to a greater extent with the melted fat, and some of the constituents of the juice in this part suffer a change, which gives rise to the peculiar flavour of roast meat. The brown sapid substance thus produced has been called *osmazome*, but nothing is really known of its true nature. In salting meat, for the purpose of preserving it, a great deal of the juice of flesh oozes out, and a proportionate loss of nutritive matter is sustained.

587. *Urine* always contains a large proportion of alkaline and earthy salts, especially of sodium chloride, phosphate and sulphate of potassium, and phosphates of calcium, magnesium, and ammonium.

The average composition of human urine may be thus stated—

Water	956.80
Urea	14.23
Uric acid	0.37
Mucus	0.16
Hippuric acid, kreatinine, ammonia, colouring matter, and unknown organic matters	15.03
Chloride of sodium	7.22
Phosphoric oxide (P_2O_5)	2.12
Potash	1.93
Sulphuric oxide (SO_3)	1.70
Lime	0.21
Magnesia	0.12
Soda	0.05
	999.94

CHEMISTRY OF VEGETATION.

588. The ultimate elements of plants, that is, the substances with which plants must be supplied in one form or other, to sustain their growth, are carbon, hydrogen, nitrogen, oxygen, sulphur, phosphorus, chlorine, silicon, potassium, sodium, calcium, magnesium, iron, manganese.

Of these, the carbon, hydrogen, nitrogen, oxygen, sulphur, and phosphorus are grouped together to form the various organic compounds furnished by plants, the remaining elements being arranged generally in the following forms:—

Chlorides and silicates of potassium and sodium, calcium sulphate, phosphates of iron (manganese?), calcium, magnesium, and ammonium, organic salts of potassium, sodium, and calcium.

Plants are capable of receiving food, either in the form of gas through the instrumentality of their leaves, or in solution by their roots.

The carbon, which is their most important constituent as regards quantity, is taken up in the form of carbonic acid gas by both these organs of the plant. This carbonic acid is derived either from the surrounding atmosphere, or from the decay of the organic matters contained in the soil which surrounds the roots of the plant.

The hydrogen is derived, partly from water, and partly from the ammonia which is carried down to the roots of the plant by rain, or is evolved in the putrefaction and decay of the nitrogenised organic matters of the soil. The ammonia also forms one great source of the nitrogen in plants, another being the nitric or nitrous acid, which is either brought down by the rain, or formed within the soil by the nitrification of the ammonia (page 132). It has been proved that atmospheric nitrogen itself is absorbed by carbohydrates such as sugar and cellulose when mixed with alkaline substances, as well as by growing fungi, decaying wood, and arable soils. As to the oxygen, it is obtained both from the carbonic acid and water, which contain this element in larger proportion than is ever present in any vegetable product. The sulphur and phosphorus contained in the organic parts of the plant appear to be chiefly derived from the sulphates and phosphates of the soil. The chlorine, silicon, and the metals are derived from the mineral constituents of the soil.

It is not difficult to imagine the course of formation of a fertile soil from a primary rock (of granite, for example) under the influence of the atmosphere and rain, exerted through a very long period.

It will be remembered that granite consists essentially of quartz (silica), felspar (silicate of aluminium and potassium or sodium), and mica (silicates of aluminium, iron, potassium, and magnesium); in addition to these, there may always be found in granite minute quantities of calcium phosphate, of sulphates, of chlorides, and of manganese.

By the disintegration of such rock under the action of air and moisture (page 83), a soil will be formed containing the various *mineral* substances required for the food of the plant. If now, upon the thin layer of soil thus formed over the face of the rock, some seeds of the lower orders of plants, the lichens, for instance, be deposited, they will grow and fructify, deriving their carbon, hydrogen, nitrogen, and oxygen from the air and rain, and their mineral constituents from the soil. The death of these lichens would add new elements of fertility to the soil, in the shape of the food which they had condensed from the air, and of the saline ingredients which had been converted within their organisation into forms better suited to sustain the higher orders of plants. Given, then, the seeds of a higher vegetation, a similar process may be supposed to take place, and at length animals would be attracted to the spot by a prospect of vegetable food, and by transporting to it elements which they had derived from other sources, would eventually confer upon it the highest fertility. The soil then coming under tillage, the crops raised upon it are consumed by animals and removed to a distance, so that the mineral food contained in the soil is by degrees exhausted, and unless it is restored the soil becomes barren.

To restore its fertility is the object of *manuring*, which consists in adding to the soil some substance which shall itself serve directly as food for the plant, or shall so modify, by chemical action, some material already present in the soil, as to convert it into a state in which the plant may take advantage of it.

As examples of substances which are added as direct food for plants, may be enumerated :—

(1) The ashes of peat, turf, coal, &c., which furnish the mineral substances originally obtained from the soil by the vegetables from which these materials were formed.

(2) Gypsum, or calcium sulphate, and magnesium sulphate, which appear to be valuable not only as sources of sulphur, calcium, and magnesium, but because they are capable of decomposing the ammonium carbonate, which is either brought down by rain or evolved by putrefaction in the soil, and of converting it into ammonium sulphate, which is retained in the soil, whereas the carbonate, being a volatile salt, would be again exhaled into the air and lost to the plants.

(3) Phosphate of lime (calcium phosphate), or bone-ash, which is most commonly converted into the soluble superphosphate (page 221), by treatment with sulphuric acid, before being employed as a manure.

(4) Sodium chloride, or common salt, serves as a source of sodium, for in contact with the calcium carbonate, which is found in all fertile soils, it is partly converted into sodium carbonate, which may in turn be converted into sodium silicate, or any other salt of sodium necessary to the growth of the plant.

(5) Sodium nitrate (Peruvian nitre) is held to be of great service in some cases, as yielding both sodium and nitrogen in a form serviceable to the plant.

(6) The silicates of potassium and sodium, which are especially useful to crops containing, like the cereals, a considerable proportion of silica in their stems; since, although that substance is contained in abundance in all soils, it is not available for the plant unless converted into a soluble state by combination with an alkali.

(7) Sulphate of ammonia (derived from the gas-works) is, of course, useful both for its sulphuric acid and ammonia.

(8) Plants, or parts of plants, ploughed into a soil, would obviously furnish food for other plants by their gradual putrefaction and decay.

(9) Bones, which furnish carbonic acid and ammonia by the putrefaction of their gelatinous matter, as well as a large supply of phosphate of lime.

(10) Urine, yielding much ammonium carbonate by the decomposition of the urea and uric acid, and an abundance of the phosphates and other saline matters required by the plant.

(11) Solid excrements of various animals, containing the insoluble salts (especially phosphates) of the animal's food, as well as easily putrescible organic matters yielding much ammonia and sulphuretted hydrogen.

(12) Guano, the dung of carnivorous sea-birds, which owes its very high value partly to the large proportion of urate of ammonia and other nitrogenised organic substances which it contains, and partly to the presence of phosphates and salts of the alkalies.

(13) Soot, which appears to act chiefly by virtue of the salts of ammonia derived from the destructive distillation of the coal.

The chief substance employed for acting chemically upon the constituents of the soil, so as to render them more serviceable to the plant, is lime, which modifies in a very important manner both the organic and mineral portions of the soil. Its action upon the former consists in promoting its decay, and the conversion of its elements into those forms, viz., carbonic acid, water, ammonia, and nitric acid, in which they may be of service to the plant. Upon the inorganic constituents of the soil, lime acts by assisting the decomposition of minerals, particularly of those which furnish the alkalies (such as felspar), and thus converting them into soluble forms.

588*a*. In some cases fertility is restored to an apparently exhausted soil, without the addition of manure, by allowing it to lie *fallow* for a time, so that under the influence of the air and moisture, such chemical changes may take place in it as will again replenish it with food available for the crops. It is not even necessary in all cases that the soil should be altogether released from cultivation; for even though it may refuse to feed any longer one particular crop, it may furnish an excellent crop of a different description, and, which is more remarkable, it may, after growing two or three different crops, be found to have regained its power of nourishing the very crop for which it was before exhausted. Experience of this has led to the adoption of the system of *rotation of crops*, by which a soil is made to yield, for example, a crop of barley, and then successive crops of grass, beans, turnips, and barley again.

The possibility of this rotation is partly accounted for by the difference in the mineral food removed from the soil by different crops; thus turnips require much of the alkalies and lime; wheat, much alkali and silica; barley, much lime and silica; and clover, much lime, so that the soil which had been exhausted for wheat, because it no longer contained enough soluble silica, might still yield sufficient alkali and lime to a crop of turnips, and when the alkali was exhausted, might furnish enough lime to a crop of clover, after which, in consequence of the chemical changes allowed by lapse of time in the soil, more of the original minerals composing it might have been decomposed and rendered available for a fresh wheat crop.

Another explanation of the benefit of systems of rotation may be given in those cases in which the refuse of the preceding crop is allowed to remain on the land. Some plants extending their roots more deeply into the soil, avail themselves of mineral food which is beyond the reach of plants furnished with shorter roots, and when the refuse of the former plants is ploughed into the land, the surface is enriched with the food collected from the subsoil.

589. Our knowledge of the chemical operations taking place in the plant, and resulting in the elaboration of the great variety of vegetable products, is very slight indeed. We appear to have sufficient evidence that sugar and starch, for example, are constructed in the plant from carbonic acid and water, that gluten results from the mutual action of the same compounds, together with ammonia, or nitric acid, and certain sulphates and phosphates, but the intermediate steps in this conversion are as yet unknown.

All seeds contain starch, gluten, or some similar nitrogenised substance (legumin, for example), together with mineral matters, these being provided for the nourishment of the young plant until its organs are sufficiently developed to enable it to procure its own food from the air or from the soil. During the process of germination, the seed absorbs oxygen and evolves carbonic acid gas, and since the albuminous constituent is the most mutable substance present, it is probably this which undergoes oxidation, and excites the conversion of the insoluble starch into soluble sugar. At this stage the seed requires, as is well known, a fair supply of water, the elements of which are required for the conversion of the starch ($C_6H_{10}O_5$) into sugar ($C_6H_{12}O_6$); water is also required to dissolve the sugar as well as the altered albuminous matter and the mineral salts, in order to form the sap of the embryo plant. These constituents of the sap, directed by the mysterious vital energy in the seed, build up the root, which extends itself in search of nourishment down into the soil, and the leaves, which discharge a similar function with respect to the air. As soon as the leaves are developed, the plant becomes able to decompose carbonic acid, water, and ammonia, to provide the organic components of its sap. Some part of these changes, at least, appears to take place in the leaves of the plant, from which, during the day-time, oxygen (together with a little nitrogen) is continually evolved. The leaves have been compared to the lungs of animals, the functions of which they reciprocate, for whilst, in the lungs of animals, an absorption of oxygen and an evolution of carbonic acid gas is observed, in the leaves of plants it is the carbonic acid gas which is absorbed and oxygen is disengaged. In the dark, plants exhale carbonic acid gas, but in much smaller quantity than they decompose in the light.

That oxygen must be evolved, if plants construct their carbonaceous compounds from carbonic acid gas and water, is obvious on reflecting that all these compounds contain less oxygen, in proportion to their carbon and hydrogen, than is contained in carbonic acid gas and water.

Thus, we may conceive the formation of all the compounds of carbon and hydrogen, or of those elements with oxygen, which are met with in plants, by the concurrence, in various proportions, of carbonic acid gas and water, and the separation of the whole or a part of their oxygen.

To take an example: cellulose ($C_6H_{10}O_5$) would result from the coalition of 6 molecules of carbonic acid gas and 5 molecules of water, with separation of 12 atoms of oxygen. Again, malic acid, $C_4H_6O_5$, would require 4 molecules of carbonic acid gas and 3 molecules of water, whilst 6 atoms of oxygen would be set free.

It is equally easy to represent the formation of nitrogenised compounds from carbonic acid gas, water, and ammonia, with separation of oxygen, for the nitrogen in all such compounds is present in so small a number of atoms relatively to the carbon and hydrogen, that the amount of oxygen separated from the carbonic acid gas and water, would always far more than suffice to convert the whole of the hydrogen of the ammonia into water, even if this hydrogen did not itself take part in the formation of the compound. Suppose, for instance, that the formation of quinine is to be accounted for—

$$20\,CO_2 + 9H_2O + 2NH_3 = \underset{\text{Quinine.}}{C_{20}H_{24}N_2O_2} + O_{47}.$$

If sulphur be a constituent of the vegetable compound to be formed, it is conceivable that the sulphuric oxide derived from the sulphates present in the soil should co-operate with the carbonic acid gas, water, and ammonia.

If the composition of gluten be correctly represented by the formula $C_{108}H_{169}N_{27}O_{34}S$, the equation explaining its formation from the above constituents of the food of the plant would be written—

$$108\,CO_2 + 44H_2O + 27NH_3 + SO_3 = C_{108}H_{169}N_{27}O_{34}S + O_{229}.$$

The chemical tendency of vegetables, therefore, is to reduce to a lower state of oxidation the substances presented in their food, whilst animals exhibit a reciprocal tendency to oxidise the materials on which they feed.

590. With respect to the last stage in the existence of the plant, the ripening of the fruit, we know a little more concerning the chemical changes which it involves. Most fruits, in their unripe condition, contain cellulose, starch, and some one or more vegetable acids, such as malic, citric, tartaric, and tannic, the latter being almost invariably present, and causing the peculiar roughness and astringency of the unripe fruit. The *characteristic* constituent of unripe fruits, however, is *pectose*, a compound of carbon, hydrogen, and oxygen, the composition of which has not been exactly determined. Pectose is quite insoluble in water, but during the ripening of the fruit it undergoes a change induced by the vegetable acids, and is converted into *pectin* ($C_{32}H_{40}O_{28}$), which is capable of dissolving in water, and yields a viscous solution. As the maturation proceeds, the pectin itself is transformed into *pectic acid* ($C_{16}H_{22}O_{15}$), and *pectosic acid* ($C_{32}H_{46}O_{31}$), which are soluble in boiling water, yielding solutions which gelatinise on cooling. It is from the presence of these acids, therefore, that many ripe fruits are so easily convertible into jellies.

Whilst the fruit remains green, its relation to the atmosphere appears to be the same as that of the leaves, for it absorbs carbonic acid gas, and evolves oxygen; but when it fairly begins to ripen, oxygen is absorbed from the air, and carbonic acid gas is evolved, whilst the starch and cellulose are converted into sugar, under the influence of the vegetable acids (page 643), and the fruit becomes sweet. It has been already seen that the conversion of starch and cellulose ($C_6H_{10}O_5$) into sugar ($C_6H_{12}O_6$) would simply require the assimilation of the elements of water, so that the absorption of oxygen and evolution of carbonic acid gas are probably necessary for the conversion of the tannic and other acids into sugar. For example—

$$\underset{\text{Tannic acid.}}{C_{14}H_{10}O_9} + H_2O + O_{12} = \underset{\text{Fruit-sugar.}}{C_6H_{12}O_6} + 8CO_2;$$

$$\underset{\text{Tartaric acid.}}{3C_4H_6O_6} + O_3 = C_6H_{12}O_6 + 3H_2O + 6CO_2.$$

When the sugar has reached the maximum, the ripening is completed; and if the fruit be kept longer, the oxidation takes the form of ordinary decay.

591. The scheme of natural chemistry would not be complete unless provision were made for the restoration of the constituents of plants, after death, to the atmosphere and soil, where they might afford food to new generations of plants. Accordingly, very shortly after the death of a plant, if sufficient moisture be present, the spores of ferments acquired from the air begin to develop, the changeable nitrogenised (albuminous) constituents begin to putrefy, and the change is commununicated to the other parts of the plant, under the form of decay, so that the plant is slowly consumed by the atmospheric oxygen, its carbon being reconverted into carbonic acid, its hydrogen into water, and its nitrogen into ammonia, these substances being then transported in the atmosphere to living plants which need them, while the mineral constituents of the dead plants are washed into the soil by rain.

Moist wood is slowly converted by decay into a brown substance, which has been called *humus*, and forms the chief part of the organic matter in soils. Alkalies dissolve this substance, and on the addition of an acid to the brown solution, a brown precipitate is obtained, which is said to contain *humic*, *ulmic*, and *geic* acids, but these substances do not crystallise, and their existence as definite acids appears to be somewhat doubtful. Two other acids of a similar kind, *crenic* and *apocrenic acids* (κρήνη, *a well*), have been obtained from the same source, and are also found occasionally in mineral waters.

When it is desired to preserve wood from decay, it is impregnated with some substance which shall form an unchangeable compound with the albuminous constituents of the sap. Kreasote (page 638) and corrosive sublimate (*kyanising*) are occasionally used for this purpose, the wood being made to imbibe a diluted solution of the preservative, either by being soaked in it or under pressure.

In *Boucherie's process* for preserving wood, the natural ascending force of the sap is ingeniously turned to account in drawing up the preservative solution. A large incision being made around the lower part of the trunk of the growing tree, a trough of clay is built up around it, and filled with a weak solution of sulphate of copper, peracetate of iron, or calcium chloride. Even after the tree has been felled, it may be made to imbibe the preserving solution, whilst in a horizontal position, by enclosing the base of the trunk in an impermeable bag supplied with the liquid from a reservoir. The impregnation of the wood with such solutions not only prevents chemical decay, but renders it less liable to the attacks of insects and the growth of fungi.

NUTRITION OF ANIMALS.

592. Between the chemistry of vegetable and that of animal life there is this fundamental distinction, that the former is eminently constructive and the latter destructive. The plant, supplied with compounds of the simplest kind—carbonic acid, water, and ammonia—constructs such complex substances as albumen and sugar; whilst the animal, incapable of deriving sustenance from the simpler compounds, being fed with those of a more complex character, converts them eventually, for the most part, into the very materials with which the constructive work of the plant commenced. It is indeed true, that some of the substances deposited in the animal frame, such as fibrin and gelatinous matter, rival in complexity many of the products of vegetable life; but for the elaboration of these substances, the animal must receive food somewhat approaching them in chemical composition. It is to this nearer resemblance between the food of animals and the proximate constituents of their frames, that we may partly ascribe the greater extent of our knowledge on the subject of the nutrition of animals, which is, however, far from being complete.

The *ultimate* elements contained in the animal body are the same as those of the vegetable, but the *proximate* constituents are far more numerous and varied.

The bones containing the phosphates and carbonates of calcium and magnesium, together with gelatinous matter, require that the animal should be supplied with food which, like bread, contains abundance of phosphates, as well as the nitrogenised matter (gluten) from which the gelatinous substance may be formed. In milk, the food of the young animal, we have also the necessary phosphates, whilst the casein affords the supply of nitrogenous matters.

Muscular flesh finds, in the gluten of bread and the casein of milk, the nitrogenised constituent from which its fibrin might be formed with even less transformation than is required for the gelatinous matter of bone, since the composition of fibrin, gluten, and casein is very similar. The albumen and fibrin of the blood have also their counterparts in the gluten and casein of bread and milk, whilst all the salts of the blood may be found in either of these articles of food.

Bread and milk, therefore, may be taken as excellent representatives of the food necessary for animals, and the same constituents are received in their flesh diet by animals which are purely carnivorous, but the flesh contains them in a more advanced stage of preparation.

It is natural to suppose that the fat, which contains no nitrogen, should be supplied by those constituents of the food which are free from that element, such as the starch in bread and the sugar and fat in milk.

Before the food can be turned to account for the sustenance of the body, it must undergo *digestion*, that is, it must be either dissolved or otherwise reduced to such a form that it can be absorbed by the blood, which it accompanies into the lungs to undergo the process of *respiration*, and thus to become fitted to serve for the *nutrition* of the various organs of the body, since these have to be continually repaired at the expense of the constituents of the blood.

The first step towards the digestion of the food is its disintegration, effected by the teeth with the aid of the *saliva*, by which it should be reduced to a pulpy mass. The saliva is an alkaline fluid characterised by the presence of a peculiar albuminous substance called *ptyalin* (*πτύω, to spit*), which easily putrefies. The action of saliva in mastication is doubtless in great part a mechanical one, but it is possible that its alkalinity assists the process chemically, by partly emulsifying the fatty portions of the food. The liability of ptyalin to putrefaction favours the supposition that it may act in some way as a ferment in promoting the digestion. This disintegration of the food is of course materially assisted by the cooking to which it has been previously subjected, the hard and fibrous portions having been thereby softened.

The food now passes to the stomach, it which it remains for some time, at the temperature of the body (98° F.), in contact with the *gastric juice*, the chief chemical agent in the digestive process. The gastric juice, which is secreted by the lining membrane of the stomach, is an acid liquid, containing hydrochloric and lactic acids. It is characterised by the presence of a peculiar substance belonging to the albuminous class of bodies, which is called *pepsin* (*πέπτω, to digest*), and possesses the remarkable power of enabling dilute acids, by its mere presence, to dissolve such substances as fibrin and coagulated albumen, which would resist the action of the acid alone for a great length of time.

An imitation of the gastric juice may be made by digesting the mucous membrane of the stomach for some hours in warm very dilute hydrochloric acid. The acid liquid thus obtained is capable of dissolving meat, curd, &c., if it be maintained at the temperature of the body. The pepsin prepared from the stomach of the pig and other animals is sometimes administered medicinally in order to assist digestion.

The principal change which the food suffers by the action of the gastric juice is the conversion of the fibrinous and albuminous constituents into soluble forms (*peptones*); the starch is also partly converted into dextrin and sugar, but the fatty constituents are unchanged.

The food which has thus been partially digested in the stomach is called by physiologists *chyme*, and passes thence into the commencement of the intestines (the *duodenum*), where it is subjected to the action of two more chemical agents, the *bile* and the *pancreatic juice*.

593. *Bile* consists essentially of a solution of two salts known as glycocholate and taurocholate of sodium. Both glycocholic and taurocholic acids are resinous, and do not neutralise the alkali, so that the bile has a strong alkaline character. Another characteristic feature of this secretion is the large proportion of carbon which it contains. *Glycocholic acid* contains 67 per cent. of carbon, whilst *taurocholic acid* contains 61 per cent.

The special function of the bile in the digestion of the food has not been explained, but from its strongly alkaline reaction it does not appear improbable that it assists in the digestion of fatty substances.

The *pancreatic juice* is another alkaline secretion which differs from the bile in containing a considerable quantity of albumen, and is very putrescible. Its particular office in digestion appears to consist in promoting the conversion of the starchy portions of the food into sugar (page 643), though it also has a powerful action upon the fats, causing them to form an intimate mixture, or emulsion, with water, and partly saponifying them. The digestion of the starch and sugar is completed by the action of the *intestinal fluid* in the further passage of the food through the intestines, so that when it arrives in the small intestines, all the soluble matters have become converted into a thin milky liquid called *chyle*, which has next to be separated mechanically from the insoluble portions, such as woody fibre, &c., which are excreted from the body.

This separation is effected in the small intestines by means of two distinct sets of vessels, one of which (the *mesenteric veins*) absorbs the dissolved starchy portions of the food, and conveys them to the liver, whence they are afterwards transferred to the right auricle of the heart. The other set of vessels (*lacteals*) absorbs the digested fatty matters, and conveys them, through the thoracic duct, into the subclavian vein, and thence at once into the right auricle of the heart.

From the right auricle this imperfect blood passes into the right ventricle of the heart, and is there mixed with the blood returned from the body by the veins, after having fulfilled its various functions in the system. The mixture, which has the usual dark brown colour of venous blood, is next forced, by the contraction of the heart, into the lungs, where it is distributed through an immense number of extremely fine vessels traversing the lungs, in contact with the minute tubes containing the inspired air, so that the venous blood is only separated from the air by very thin and moist membranes. Through these membranes the dark venous blood gives up the carbonic acid gas with which it had become charged by the oxidation of the carbon of the organs in its passage through the body, and acquires, in return, about an equal volume of oxygen, which converts it into the bright crimson arterial blood. In this state it returns to the left side of the heart, whence it is conveyed, by the arteries, to the different organs of the body. The chemistry of the changes effected and suffered by the blood in its circulation through the body is very imperfectly understood. One of its great offices is the supply of the oxygen necessary to oxidise the components of the various organs, and thus to evolve the heat which maintains the body at its high temperature. The results of the oxidation of these organs are undoubtedly very numerous; among them we may trace carbonic, sulphuric, phosphoric, lactic, butyric, and uric acids, as well as urea and some other substances. The destroyed tissues must at the same time be replaced by the deposition, from the blood, of fresh particles similar to those which have been oxidised. In the course of the blood through the circulation, the above products of oxidation have to be removed from it—the carbonic acid by the lungs and skin—the sulphuric, phosphoric, and uric acids, and the urea, by the kidneys.

The various liquid secretions of the body, such as the bile, the saliva, the gastric juice, &c., have also to be elaborated from the blood during its circulation through the arteries, after which it returns, by the veins, to the heart, to have its composition restored by the matters derived from the food, and to be reconverted into arterial blood in the lungs.

When it is remembered that the body is exposed to very considerable variations of external heat and cold, a question occurs as to the provision made for maintaining it at its uniform temperature. This is effected through the agency of the fat which is deposited in all the organs of the body. Since fatty substances in general are particularly rich in carbon and hydrogen, their oxidation within the body would be attended with the production of more heat than that of those parts of the organs which contain much nitrogen and oxygen. Accordingly, when the body is exposed to a low temperature, a larger quantity of its fat is consumed by the oxidising action of the blood, and a corresponding increase takes place in the amount of heat evolved, thus compensating for the greater loss of heat suffered by the body in the cooler atmosphere. Of course, in cold weather, when more oxygen is required to maintain the heat of the frame, a larger quantity of that gas is inhaled at each breath, on account of the higher specific gravity of the air, in addition to which, we have the quickened respiration which always attends exposure to cold. To supply this extra demand for carbon and hydrogen in cold weather, we instinctively have recourse to such substances as fat, starch, sugar, &c., which contain them in large proportion, and these aliments, free from nitrogen, are often spoken of as the *respiratory constituents* of food; whilst flesh, gluten, albumen, &c., which contain nitrogen, are styled the *plastic* elements of nutrition (*πλάσσω, to form*).

Bearing in mind that the food has a two-fold office—to nourish the frame and to maintain the animal heat—it will be evident that a judiciously regulated diet will contain due proportions of these nitrogenous constituents, such as albumen, fibrin, and casein, which serve to supply the waste of the organs, and of such non-nitrogenised bodies as starch and sugar, from which fat may be elaborated to sustain the bodily warmth.

The proportion which these two parts of the food should bear to each other will, of course, depend upon the particular condition of existence of the animal. Thus, for a growing animal, a larger proportion of the nitrogenised or plastic portion of food would be required than for an animal whose growth has ceased; and animals exposed to a low temperature would require more of the non-nitrogenised or heat-giving portions of the food.

Accordingly, we find that a man can live upon a diet which contains (as in the case of wheaten bread) 5 parts of non-nitrogenised (starch and sugar) to 1 part of nitrogenised food (gluten); whilst an infant, whose increasing organs require more nitrogenised material, thrives upon milk, in which this amounts to 1 part (casein) for every 4 parts of the non-nitrogenised portion (milk-sugar and fat). The inhabitants of cold climates consume, as is well known, much more oil and fat than those of the temperate and hot regions.

An examination of the composition of different articles of food affords us an explanation of the custom which experience has warranted, of associating particular varieties of food. Thus, assuming as our standard of comparison the composition of bread, which contains one of nutritive to five of heat-giving matter, the propriety of eating potatoes (1 nutritive : 10 heat-giving) with beef (1 nutritive : 1.7 heat-giving), and rice (1 : 12.3), with mutton (1 : 2.7) will be appreciated.

All muscular or mental exertion is attended with a corresponding oxidation of the tissues of the frame, just as each movement of a steam-engine may be traced to the combustion of a proportionate quantity of coal under the boiler; and hence such exertion both creates a demand for food, and quickens the respiration to obtain an increased supply of oxygen.

CHANGES IN THE ANIMAL BODY AFTER DEATH.

594. After the death of animals, just as after that of plants, a change takes place in some of the nitrogenous constituents, attended by the development of living organisms of a very low order, and this change is soon communicated to all parts of the body, which undergo a putrefaction or metamorphosis, of which the ultimate results are the conversion of the carbon into carbonic acid, the hydrogen into water, the nitrogen into ammonia, nitrous and nitric acids, and the sulphur into sulphuretted hydrogen and sulphuric acid. The mineral constituents of the animal frame then mingle with the surrounding soil, and are ready to take part in the nourishment of plants, which construct the organic components of their frames from the carbonic acid and ammonia furnished by the putrefaction of the animal, and then serve in their turn as sustenance for animals whose respiration supplies the air with carbonic acid gas and takes in exchange the oxygen eliminated by the plant.

The functions of the two divisions of animate nature are, therefore, perfectly reciprocal, and this relationship must be regarded as the foundation of economical agriculture. If it were possible to prevent the change of the atmosphere, it is quite conceivable that a perpetual succession of plants and animals could be raised upon a given farm without any importation of food, provided that there was also no exportation. Or even, permitting an exportation of food, the succession of plants and animals raised upon the same land might be, at least, a very long one, if the solid and liquid excrements of the animals, to feed whom this exportation took place, were restored to the land upon which this food was raised. The explanation of this is, that the solid and liquid excrements of the animal contain a very large proportion of the mineral constituents of the soil, in the very state in which they are best fitted for assimilation by the crop, and as long as the soil contains the requisite supply of mineral food, the plant can derive its organic constituents from the atmosphere itself.

Forasmuch, however, as the vegetable and animal food produced upon a farm is generally exported to feed the dwellers in towns, whose excrements cannot, without excessive outlay, be returned to the soil whence the food was derived, it becomes necessary for the agriculturist to purchase farm-yard manure, guano, &c., in order to prevent the exhaustion of his soil. A great manufacturing country, in which the majority of the inhabitants are congregated in very large numbers around a few centres of industry, at a distance from the land under tillage, is thus of necessity dependent for a considerable proportion of its food upon more thinly populated countries where manufactures do not flourish, to which it exports in return the produce of the labour which it feeds.

The parts of the frames of animals differ very considerably in their tendency to putrefaction. The blood and muscular flesh undergo this change most readily, as being the most complex parts of the body, whilst the fat remains unchanged for a much longer period, and the bones and hair will also resist putrefaction for a great length of time. The comparative stability of the fat is observed in the bodies of animals which have been buried for some time in a very wet situation, when they are often found converted almost entirely into a mass of *adipocere*, consisting of the palmitic and margaric acids derived from the fat.

When an animal body is thoroughly dried, it may be preserved unchanged for any length of time, and this is the simplest of the methods adopted for the preservation of animal food, becoming far more efficacious when combined with the use of some antiseptic substance, such as salt, sugar, spice, or kreasote. The preservative effects of salt and sugar are sometimes ascribed to the attraction exerted by them upon moisture, which they withdraw from the flesh, whilst spices owe their antiseptic power to the essential oils, which appear to have a specific action in arresting fermentative change, a character which also belongs to kreasote, carbolic acid, and probably to other substances which occur in the smoke of wood, well known for its efficacy in *curing* animal matter. Such substances are often called *anti-zymotic* bodies; carbolic, salicylic, benzoic, and boracic acids are classed under this head.

A process commonly adopted for the preservation of animal and vegetable food, consists in heating them with a little water in tin canisters, which are sealed air-tight as soon as the steam has expelled all the air, and if the organic matter be perfectly fresh, this mode of preserving it is found very successful, though, if putrefaction has once commenced, to ever so slight an extent, it will continue even in the sealed canister quite independently of the air.

Modern experiments have disclosed a great imperfection in our acquaintance with the conditions under which putrefaction takes place, and indicate the presence in the atmosphere of some minute solid particles which appear to be minute ova or germs, and have the power of inducing the commencement of this change. It has been found that milk, for example, may be kept for a very considerable period without putrefying, if it be boiled in a flask, the neck of which is afterwards loosely stopped with cotton wool, whilst, if the plug of cotton wool be omitted, the other conditions being precisely the same, putrefaction will take place very speedily.

Perfectly fresh animal matters have also been preserved for a length of time in that state, in vessels containing air which has been passed through red hot tubes with the view of destroying any living germs which might be present, and such substances have been found to putrefy as soon as the unpurified air was allowed access to them.

The extremes of the scale of animated existence would appear to meet here. The highest forms of organised matter, immediately after death, serve to nourish some of the lowest orders of living germs, these helping to resolve the complex matter into the simpler forms of carbonic acid, ammonia, &c., which are returned to the atmosphere, the great receptacle for the four chief elements of living matter, carbon, hydrogen, nitrogen, and oxygen.

CONSTITUTION OF ORGANIC COMPOUNDS.

595. It has been seen in the preceding pages that organic compounds which differ widely from each other in their chemical properties may yet have the same molecular weight and the same chemical composition, and it has been pointed out that the difference in their properties is due to a difference in the groups into which the carbon, hydrogen, nitrogen, and oxygen atoms are distributed. But there are some compounds containing the same groupings of the atoms, yet differing in their properties, because these groupings (or radicals) occupy different positions in relation to each other; this is referred to in the phrase *position-isomerism.*

There is only one compound having the formula CH_4, methane or marsh-gas, and this yields only one compound when one of its hydrogen atoms is replaced by another radical, showing that each of its four hydrogen atoms stands in the same relation to the carbon atom; thus, if one hydrogen atom be replaced by Cl, we obtain CH_3Cl, mono-chloro-methane or methyl chloride, which has always the same properties, however it may be prepared, so that CHHHCl, CHHClH, CHClHH, and CClHHH, represent one and the same substance.

It is in order to express, and to attempt to explain, this equality of position of the hydrogen atoms in relation to the carbon, that they are often represented on paper as symmetrically arranged round the central carbon atom (fig. 288*a*), so that which ever H is replaced by Cl, the figure has only to be turned round in order to appear the same. On paper, the atoms are, of necessity, written on the same plane, but it is not to be supposed that this represents their arrangement in the molecule. At present we have no satisfactory knowledge of the shapes of molecules, but we are obliged to think of them as having three dimensions. The hydrogen atoms of CH_4 may possibly be arranged symmetrically on the surface of a sphere with the C at the centre, or they may be situated at the four angles on the base of a regular tetrahedron with the carbon at the vertex.

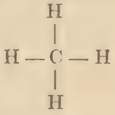


Fig. 288*a*.—Methane.

In the explanations which follow, no assumption will be made as to the true figures of the molecules, it will only be attempted to convey the idea of position by arranging the atoms on the same plane.

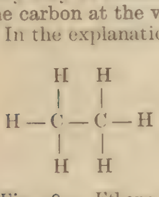


Fig. 289.—Ethane.

If methyl, CH_3, instead of Cl, be substituted for an atom of H in CH_4, the same reasoning holds good, that there can be only one compound of the formula $CH_3(CH_3)$ or C_2H_6, ethane, because, whichever of the hydrogen atoms is replaced by CH_3, this group will always stand in the same relative position to the carbon-atom and to the other three hydrogen atoms (fig. 289). Again, the symmetry of the figure of ethane shows that whichever of its hydrogen atoms is replaced by methyl, it will have the same relative position to the carbon atoms and to the remaining hydrogen atoms of ethane, and that there can only be one hydrocarbon of the formula $CH_3.CH_2(CH_3)$ or C_3H_8, propane (fig. 290). But, in propane, all the hydrogen atoms are not in exactly the same relative positions in respect to the three atoms of carbon, so that if methyl be substituted for hydrogen in the CH_2 part of the figure, we shall have a different compound from that produced by effecting the substitution in either of the CH_3 parts; one compound having the formula $CH_3.CH(CH_3).CH_3$, and the other, $CH_2(CH_3).CH_2.CH_3$,

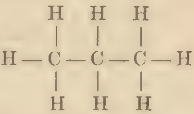


Fig. 290.—Propane.

or $CH_3.CH_2.CH_2(CH_3)$ which is the same thing. Both compounds have the empirical formula C_4H_{10} and are called *isomeric butanes.*

596. The butane described at page 471 is *normal butane,* so termed from *norma, a rule,* because it has the properties which butane ought to possess from its position in the homologous series of paraffins, and is obtained by the process which would be expected to furnish it, viz., by the action of zinc upon ethyl iodide. For ethyl iodide, C_2H_5I is the iodine substitution-product of ethane, $CH_3.CH_3$, and its formula is $CH_3.CH_2I$. When the diad zinc acts upon this, it must take the I_2, which it requires to form the iodide, from two molecules of ethyl iodide, leaving the residues to combine and produce butane; thus—

$$CH_3.CH_2I + Zn + ICH_2.CH_3 = ZnI_2 + CH_3.CH_2.CH_2.CH_3,$$

which is the formula of normal butane.

Iso-butane (*ἴσος, equal*), C_4H_{10}, is not liquefied under $-17°$ C., while normal butane is liquefied at 1° C. It is obtained by the action of zinc and water upon *tertiary butyl-iodide;* $CH_3.C(CH_3)I.CH_3 + H_2O + Zn = CH_3.C(CH_3)H.CH_3 + HI + ZnO$. The difference in the arrangement of the atoms in normal butane and isobutane is seen in figs. 291, 292.

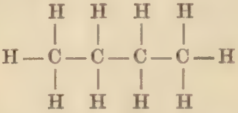


Fig. 291.—Normal butane.

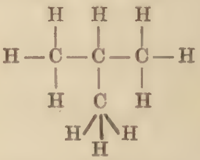


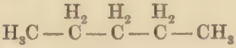
Fig. 292.—Iso-butane.

The atoms of pentane, C_5H_{12}, may be arranged so as to produce three different compounds. The pentane described at p. 472 is the normal pentane $CH_3(CH_2{}_3CH_3$, and boils at 38° C.; *iso-pentane,* $CH_3.CH_2.CH(CH_3)_2$, boils at 30°, and is obtained by the action of zinc and water upon *secondary iso-amylic iodide,* $CH_3.CHI.CH(CH_3)_2$. *Neo-pentane* (*νέος, new*) or *tetra-methyl-methane,* $C(CH_3)_4$ boils at 9°.5 C., and is prepared by the action of zinc-methyl on *tertiary butylic iodide*—

$$Zn(CH_3)_2 + 2C(CH_3)_3I = 2C(CH_3)_4 + ZnI_2$$

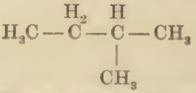
a mode of formation which indicates the presence of four methyl groups in neopentane. Figs. 293, 294, 295, indicate the relation between the three pentanes.

It will be evident that, as the number of carbon atoms in the hydrocarbon increases, the greater the variety of arrangement, and therefore the greater the number of possible isomerides. Thus, there may be discovered 800 compounds having the formula $C_{13}H_{28}$.



$$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-CH_3$$

Fig. 293.—Normal pentane.



$$H_3C-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

Fig. 294.—Iso-pentane.

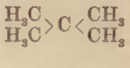


Fig. 295.—Neo-pentane.

Normal paraffins are those in which all the carbon atoms are united in a single chain without branches, so that the formula begins and ends with CH_3, every other link being CH_2 (fig. 293).

Iso-paraffins, or *secondary paraffins,* have at least one branch, that is, at least one carbon atom is united with more than two other carbon atoms, as in fig. 294.

Neo-paraffins, or *tertiary paraffins,* have at least one carbon atom united to four others, as in fig. 295.

That this is really the constitution of neopentane, is shown by the steps for obtaining it synthetically; acetone, $H_3C(CO)CH_3$, treated with PCl_5, yields $H_3C(CCl_2)CH_3$, and this, acted on by zinc-methyl, gives $H_3C(C(CH_3)_2)CH_3$ or neo-pentane.

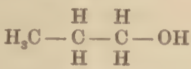
597. *Isomeric alcohols.*—Since alcohols are formed from paraffins by replacing hydrogen by hydroxyle, the isomeric paraffins yield corresponding alcohols. Methane and ethane yield only normal alcohols, because, whichever hydrogen atom is replaced by hydroxyle, the same compound will result.

Normal, or primary alcohols, are derived from the normal paraffins by the replacement of the H of a CH_3 group by OH.

Thus, normal propane, $H_3C.CH_2.CH_3$, yields normal propyl-alcohol—

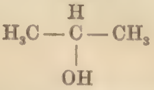
$$H_3C.CH_2.CH_2.OH\ ;$$

hence the formulæ of the primary alcohols begin with H_3C and end with $CH_2.OH$, and the hydroxyle group is united to a carbon atom which is linked to only one other carbon atom (fig. 296).



$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$$

Fig. 296.—Normal propyl alcohol.



$$H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

Fig. 297.—Isopropylic alcohol.

The *secondary alcohols* are formed from the normal paraffins by the replacement of the H in the CH_2 part of the formula by OH.

Thus, *secondary propyl-alcohol*, or *isopropylic alcohol*, is $H_3C.CH(OH).CH_3$ or $(CH_3)_2.CH.OH$.

In the secondary alcohols, therefore, the hydroxyle group is united to a carbon atom which is linked to two other carbon atoms (fig. 297).

Normal propyl alcohol has been described at p. 492. Its normal character is shown by its boiling point, 97° C., which is 19° above that of its lower homologue, ethyl-alcohol, and 19° below that of its higher homologue, butyl-alcohol.

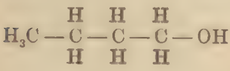
Iso-propylic alcohol boils at 84° C., and its sp. gr. is 0.79. It is obtained by acting upon acetone with the nascent hydrogen furnished by water and sodium-amalgam; $H_3C.CO.CH_3 + 2H = H_3C.CH.OH.CH_3$, a reaction which confirms the above view of its constitution.

The secondary alcohols do not yield aldehyds by partial oxidation, like the primary alcohols, but they are converted into ketones; thus, iso-propylic alcohol, distilled with a diluted mixture of sulphuric acid and potassium dichromate is oxidised to acetone; $H_3C.CH.OH.CH_3 + O = H_3C.CO.CH_3 + H_2O$. The results of the further oxidation of the ketones are described at p. 545.

Secondary propyl-alcohol is remarkable for combining with water to form $(C_3H_8O)_2.H_2O$, which has the same percentage composition as ethyl-alcohol, and nearly the same boiling point (80°); but when acted on by iodine and phosphorus, it is converted into isopropylic iodide, $H_3C.CHI.CH_3$, while ethyl-alcohol yields ethyl iodide, $H_3C.CH_2.I$.

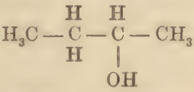
The *tertiary alcohols* are formed from the iso-paraffins, by the replacement of the H in the CH part of the formula by OH. Thus, isobutane, $CH_3.CH(CH_3).CH_3$, yields *tertiary butylic alcohol*, $CH_3.COH.CH_3.CH_3$, or $(CH_3)_3C.OH$.

In the tertiary alcohols, therefore, the hydroxyle group is united to a carbon atom which is linked to three other carbon atoms (fig. 300). Figs. 298, 299, and 300 show the relations between a primary, secondary, and tertiary alcohol.



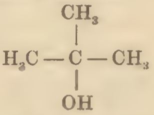
$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$$

Fig. 298.—Primary butyl-alcohol.



$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CH_3$$

Fig. 299.—Secondary butyl-alcohol.

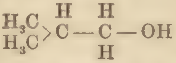


$$H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

Fig. 300.—Tertiary (iso) butyl-alcohol.

Since the carbon to which the hydroxyle is united is linked to three other carbon atoms, there can be no normal tertiary alcohols (in which the carbon atoms are united in a single chain), so that the tertiary alcohols are always iso-alcohols.

598. Normal primary butyl-alcohol has been described at page 492, together with fermentation butyl-alcohol, which is the *primary isobutylic alcohol* (fig. 301).



$$\begin{matrix}H_3C\\H_3C\end{matrix}>\overset{H}{C}-\overset{H}{\underset{H}{C}}-OH$$

Fig. 301.—Primary iso-butylic-alcohol.

Secondary butyl-alcohol is obtained by several steps from ethyl-ether, $CH_3.CH_2.O.C_2H_5$. (1) Chlorine acting upon ether in cold and darkness, converts it into *dichlorether*, $CH_2Cl.CHCl.O.C_2H_5$. (2) Zinc ethide converts this into *ethyl-chlorether*—

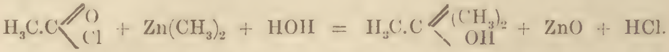
$$Zn(C_2H_5)_2 + 2(CH_2Cl.CHCl.O.C_2H_5) = ZnCl_2 + 2(CH_2Cl.CH.C_2H_5.O.C_2H_5).$$

(3) This last, when heated with HI, yields *secondary butyl iodide*—

$$CH_2Cl.CH(CH_2.CH_3).O.C_2H_5 + 4HI = CH_3.CH(CH_2.CH_3)I + HCl + H_2O + C_2H_5I + I_2.$$

(4) The iodide is converted into the acetate by heating it with potassium acetate, and the acetate, when decomposed by potash, furnishes the secondary butyl-alcohol as a liquid of sp. gr. 0.85, and boiling point 97° C.

Tertiary butyl-alcohol may be prepared by acting on acetyl chloride with zinc methide, and treating the solid product with water, the final result being expressed by the formula—



$$H_3C.C\begin{cases}O\\Cl\end{cases} + Zn(CH_3)_2 + HOH = H_3C.C\begin{cases}(CH_3)_2\\OH\end{cases} + ZnO + HCl.$$

Tertiary butyl-alcohol is a crystalline solid, fusing at 25° C., and boiling at 83° C. It is deliquescent, and forms a stable aquate $(C_4H_{10}O)_2.Aq$. It has a peculiar camphor-like smell, and is present in some fousel oils. Oxidising agents convert it into carbonic, acetic, and isobutylic acids.

As in the case of the hydrocarbons, the number of alcohols having the same empirical formula must increase with the number of carbon atoms; thus, there have been already obtained three primary, three secondary, and one tertiary amyl-alcohols.

Greater facility in naming these numerous compounds is attained by taking methyl-alcohol or carbinol as the starting-point, and supposing the alcohols to be derived from it by substitution of alcohol-radicals for the hydrogen in the methyl group. Then, the primary alcohols will be mono-substitution derivatives of carbinol, as shown in the following formulæ:

Carbinol, $CH_3.OH$. Primary propyl-alcohol, or ethyl-carbinol, $CH_2.C_2H_5.OH$. Primary butyl-alcohol, or propyl-carbinol, $CH_2.C_3H_7.OH$. Primary iso-butyl-alcohol, or iso-propyl-carbinol, $CH_2.C_3H_7.OH$ (the difference here consisting in propyl, $CH_2(CH_2CH_3)$, formed by the methylation of ethyl, $CH_2(CH_3)$, and *iso-propyl*, $CH(CH_3)_2$, formed by the di-methylation of methyl).

The secondary alcohols may be regarded as di-substitution products of carbinol; secondary propyl-alcohol or *di-methyl-carbinol*, $CH(CH_3)_2.OH$, is evidently identical with iso-propyl-alcohol. Secondary butyl-alcohol is *ethyl-methyl-carbinol*, $CH.C_2H_5.CH_3.OH$. Secondary amylic alcohol is *methyl-propyl-carbinol*—

$$CH.CH_3.C_3H_7.OH.$$

Another secondary amylic alcohol is *di-ethyl-carbinol*, $CH(C_2H_5)_2.OH$. The tertiary alcohols would be tri-substitution products of carbinol. Tertiary butyl-alcohol is *tri-methyl-carbinol*, $C(CH_3)_3.OH$. Tertiary amyl-alcohol is *ethyl-dimethyl-carbinol*, $C(C_2H_5)(CH_3)_2.OH$.

599. *To distinguish between primary, secondary, and tertiary alcohols.*—(1) When acted on by oxidising agents, a primary alcohol yields an aldehyd, containing the same number of carbon atoms as the alcohol; thus, ethyl-alcohol, $CH_2.CH_3.OH$, yields ethyl-aldehyd, $CH_3.COH$. A secondary alcohol yields a ketone containing the same number of carbon atoms; thus, secondary propyl-alcohol, $CH(CH_3)_2.OH$, yields di-methyl ketone, $CH_3.CO.CH_3$; a tertiary alcohol is either broken up into two or more acids containing less carbon, or it may give rise to a ketone containing one atom less carbon than itself, the atom of carbon being oxidised to carbonic or formic acid; thus, tertiary butyl-alcohol, $C(CH_3)_3.OH$, yields acetone, $(CH_3)_2.CO$, and formic acid.

(2) The alcohol is converted into the corresponding iodide by distilling with iodine and phosphorus (see p. 553); the iodide is distilled with a mixture of silver nitrite with dry sand (to dilute it), when the corresponding nitro-paraffin is obtained; thus, ethyl iodide yields nitro-ethane, $(C_2H_5NO_2)$—

$$CH_2.CH_3.I + AgNO_2 = CH_2.CH_3.NO_2 + AgI.$$

The distillate is mixed with potassium nitrite and weak potash, and dilute sulphuric acid is gradually added; if the alcohol be primary, a *red* solution of the corresponding potassium nitrolate will be obtained, the nitro-paraffin having been converted into the corresponding *nitrolic acid*, by the nitrous acid; thus, nitroethane yields nitrolic acid—

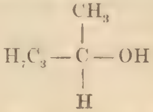
$$CH_2.CH_3.NO_2 + HNO_2 = CH.NO.CH_3.NO_2 + H_2O.$$

Nitrolic acids are colourless, but their alkaline salts have a dark red colour; they are very unstable, being decomposed into nitrous oxide and a fatty acid; thus nitrolic acid yields nitrous oxide and acetic acid—

$$CH.NO.CH_3.NO_2 = CH_3.CO_2H + N_2O.$$

If the alcohol be secondary, a *blue* solution of a *pseudonitrole* will be obtained; thus, secondary amylic alcohol, $CH.CH_3.C_3H_7.OH$, would yield the secondary nitro-paraffin, $CH.CH_3.C_3H_7.NO_2$, which would be converted by nitrous acid into the pseudonitrole, $C.NO.CH_3.C_3H_7.NO_2$, giving a blue solution. If the alcohol be tertiary, no colour is produced, the tertiary nitro-paraffins being unacted on by nitrous acid.

(3) In some cases the action of the alcohols on polarised light has been used to ascertain their constitution. Thus, the fousel oil which distils over at the end of the rectification of spirit made from grain, was long regarded as simply amyl-alcohol, $C_5H_{11}.OH$. But it was noticed that different samples of it acted differently on a ray of polarised light, some rotating the plane of polarisation to the left to a greater extent than others, indicating that they were mixtures. By dissolving them in sulphuric acid, they were converted into sulphamylic acids, $C_5H_{11}HSO_4$, and, by neutralising with barium carbonate, two barium sulphamylates were obtained, having the same composition, but one being much more soluble in water than the other. The alcohol prepared from the less soluble barium salt was without action on polarised light, and boiled at 131° C.; the other rotated the plane of polarisation strongly to the left, and boiled at about 128° C.

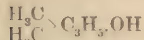


$$\begin{array}{c} CH_3 \\ | \\ H_7C_3 - C - OH \\ | \\ H \end{array}$$

Fig. 302.—Active amyl alcohol.

It is found that compounds which act on polarised light contain one or more *asymmetric* carbon atoms, that is, carbon atoms linked to four dissimilar radicals. Thus, the active amyl-alcohol is secondary amyl-alcohol, or methyl-propyl-carbinol (fig. 302), in which there is an asymmetric carbon atom linked to the four dissimilar radicals, methyl, propyl, hydroxyl, and hydrogen.

The inactive amyl-alcohol is iso-amyl-alcohol or isobutyl carbinol (fig. 303).



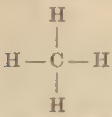
$$\left.\begin{array}{l} H_3C \\ H_3C \end{array}\right\rangle C_3H_5.OH$$

Fig. 303.—Inactive amyl-alcohol.

This is an example of *physical isomerism*, where almost the only difference between the isomerides is some physical property depending on the grouping of the atoms.

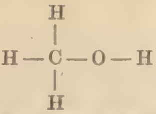
600. Derivatives of the isomeric alcohols.—The substitution of other radicals for the hydroxyl group in the alcohols gives rise, as would be expected, to the formation of primary, secondary, tertiary, and iso-alcohol derivatives. Thus, normal propyl-alcohol, $C_3H_7.OH$, yields normal propyl chloride, $C_3H_7.Cl$, while secondary or iso-propyl alcohol, $CH_3.CH.OH.CH_3$, yields *secondary* or *iso-propyl chloride*, $CH_3.CHCl.CH_3$. Tertiary iso-butyl alcohol, $C(CH_3)_3OH$ yields *tertiary iso-butyl chloride*, $C(CH_3)_3Cl$. Similar compounds are formed by chlorine, bromine, and iodine from other alcohols.

The acids of the acetic series are formed from the primary alcohols by the oxidation of the group $CH_2.OH$, and its conversion into the carboxyl group, $CO.OH$; thus methyl-alcohol $HCH_2.OH$ yields formic acid $HCO.OH$, whilst the aldehyds are produced by the conversion of the $CH_2.OH$ group into a $C.O.H$ group. Figs. 304, 305, 306, 307, exhibit the relation between the hydride, the alcohol, the aldehyd, and the acid of methyl.



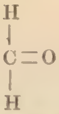
$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$$

Fig. 304.—Methane.



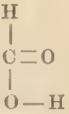
$$\begin{array}{c} H \\ | \\ H - C - O - H \\ | \\ H \end{array}$$

Fig. 305.—Methyl alcohol.



$$\begin{array}{c} H \\ | \\ C = O \\ | \\ H \end{array}$$

Fig. 306.—Methyl aldehyd.



$$\begin{array}{c} H \\ | \\ C = O \\ | \\ O - H \end{array}$$

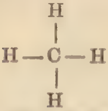
Fig. 307.—Formic acid.

It is evident that, allowing carbon to be tetrad or to have an atom-fixing power = 4, oxygen to be diad, or to have an atom-fixing power = 2, and hydrogen to be monad, or to have an atom-fixing power = 1, no other method of representing the attachment of the atoms to each other would be possible. The production of potassium formate $K.CO.OH$ by the direct union of CO with KOH strongly supports the above view of formic acid.

The synthesis of acetic acid from CH_4, $COCl_2$ and H_2O shows that acetic acid is produced by the substitution of methyl for hydrogen in formic acid. When methane is acted on by carbon oxychloride, hydrochloric acid and acetyl chloride are formed, $CH_4 + COCl_2 = HCl + C_2H_3O.Cl$, and when this is decomposed by water, acetic acid and hydrochloric acid are produced—

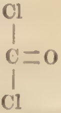
$$C_2H_3O.Cl + HOH = C_2H_3O.HO + HCl.$$

The constitution of the substances concerned is here shown (figs. 308, 309, 310, 311).



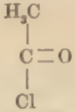
$$\begin{array}{c}H\\|\\H-C-H\\|\\H\end{array}$$

Fig. 308.—Methane.



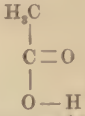
$$\begin{array}{l}Cl\\|\\C=O\\|\\Cl\end{array}$$

Fig. 309.—Carbon oxychloride.



$$\begin{array}{l}H_3C\\|\\C=O\\|\\Cl\end{array}$$

Fig. 310.—Acetyl chloride.



$$\begin{array}{l}H_3C\\|\\C=O\\|\\O-H\end{array}$$

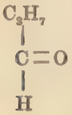
Fig. 311.—Acetic acid.

In a similar way other paraffins may be converted into the fatty acids; thus, amyl hydride $C_5H_{11}.H$ yields caproic acid, $C_5H_{11}.CO.OH$.

The oxidation of the normal primary alcohols yields the normal aldehyds and acids, but the iso-alcohols yield iso-aldehyds and acids, a few of which are known.

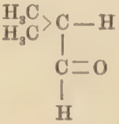
Iso-butyric aldehyd is obtained by distilling calcium iso-butyrate with calcium formate, just as butyric aldehyd is obtained from calcium butyrate.

Iso-valeric aldehyd, or *valeral*, is obtained by distilling fermentation amyl-alcohol with potassium dichromate and sulphuric acid. The constitution of these aldehyds is here represented (figs. 312, 313, 314, 315).



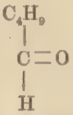
$$\begin{array}{l}C_3H_7\\|\\C=O\\|\\H\end{array}$$

Fig. 312.—Normal butyric aldehyd.



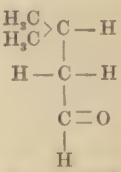
$$\begin{array}{l}\begin{matrix}H_3C\\H_3C\end{matrix}\!>C-H\\ \qquad\;|\\ \qquad C=O\\ \qquad\;|\\ \qquad H\end{array}$$

Fig. 313.—Iso-butyric aldehyd.



$$\begin{array}{l}C_4H_9\\|\\C=O\\|\\H\end{array}$$

Fig. 314.—Normal valeric aldehyd.

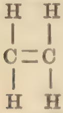


$$\begin{array}{l}\begin{matrix}H_3C\\H_3C\end{matrix}\!>C-H\\ \qquad\;|\\ \quad H-C-H\\ \qquad\;|\\ \qquad C=O\\ \qquad\;|\\ \qquad H\end{array}$$

Fig. 315.—Iso-valeric aldehyd.

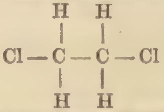
Iso-butyric and *iso-valeric* acids are obtained from the corresponding alcohols and their derivatives by processes similar to those by which the normal acids are obtained. Iso-butyric acid is found in the fruit of the carob-tree.

601. *Olefin hydrocarbons.*—These differ from the paraffin hydrocarbons in containing two of their carbon-atoms united by two atom-fixing powers, as in ethene, fig. 316. They are, therefore, *unsaturated* hydrocarbons, while the paraffins are *saturated* hydrocarbons, in which no two carbon atoms are united by more than a single bond. This difference in constitution is indicated by the disposition of ethylene (p. 472) to combine directly with two atoms of a monatomic radical, such as Cl or Br, leaving the carbon atoms united by a single bond (fig. 317).



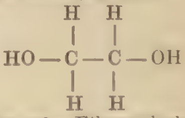
$$\begin{array}{cc}H&H\\|&|\\C&\!\!=\!\!C\\|&|\\H&H\end{array}$$

Fig. 316.—Ethene.



$$\begin{array}{ccccccc}&&H&&H&&\\&&|&&|&&\\Cl&-&C&-&C&-&Cl\\&&|&&|&&\\&&H&&H&&\end{array}$$

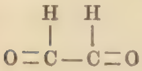
Fig. 317.—Ethene dichloride.



$$\begin{array}{ccccccc}&&H&&H&&\\&&|&&|&&\\HO&-&C&-&C&-&OH\\&&|&&|&&\\&&H&&H&&\end{array}$$

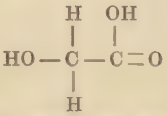
Fig. 318.—Ethene alcohol.

When ethene dibromide is decomposed by boiling solution of potassium carbonate (p. 495), the water exchanges hydroxyle for bromine, forming hydrobromic acid and ethene hydrate or glycol (fig. 318). The glycols, therefore, contain twice the same group which the monohydric alcohols contain once, viz., the group $H_2C.OH$.



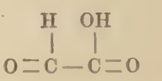
$$\begin{array}{ccccccc}&&H&&H&&\\&&|&&|&&\\O&=&C&-&C&=&O\end{array}$$

Fig. 319.—Glyoxal.



$$\begin{array}{ccccccc}&&H&&OH&&\\&&|&&|&&\\HO&-&C&-&C&=&O\\&&|&&&&\\&&H&&&&\end{array}$$

Fig. 320.—Glycolic acid.



$$\begin{array}{ccccccc}&&H&&OH&&\\&&|&&|&&\\O&=&C&-&C&=&O\end{array}$$

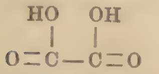
Fig. 321.—Glyoxylic acid.

The partial oxidation of the glycols converts this group into HC : O, just as it does in alcohol, but the aldehyd of glycol contains this group twice (fig. 319). The next step in the oxidation of glycol also resembles that in the case of alcohol, the group $H_2C.OH$ becoming OC.OH (fig. 320).

A further oxidation converts the remaining $H_2C.OH$ into the aldehyd group HC : O (fig. 321).

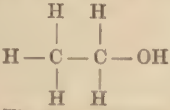
Lastly, this group is converted into OC.OH (fig. 322).

The formation of the homologous series of olefin hydrocarbons from the alcohols of the paraffins by dehydrating agents is easily explained by the removal of the HO group and an atom of H as H_2O, leaving the two liberated affinities or atom-fixing powers to hold the two carbon atoms doubly linked, as will seen by comparing figs. 323, 324.



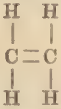
$$\mathrm{O{=}\overset{HO}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}{=}O}$$

Fig. 322.—Oxalic acid.



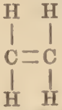
$$\mathrm{H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH}$$

Fig. 323.—Alcohol.



$$\mathrm{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}{=}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}$$

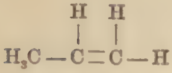
Fig. 324.—Ethene.



$$\mathrm{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}{=}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}$$

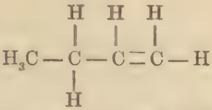
Fig. 325.—Ethylene, C_2H_4.

Just as the homologues of the paraffins are formed by the continued substitution of methyl for hydrogen in methane, so are the olefins formed from ethene by the continued removal of H and addition of CH_3, that is, by the continual addition of CH_2, or $\mathrm{\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}}$ as shown in figs. 325, 326, 327, 328.



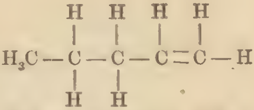
$$\mathrm{H_3C-\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}-H}$$

Fig. 326.—Propylene, C_3H_6.



$$\mathrm{H_3C-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}-H}$$

Fig. 327.—Butylene, C_4H_8.

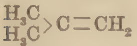


$$\mathrm{H_3C-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}-H}$$

Fig. 328.—Amylene, C_5H_{10}.

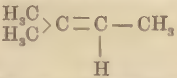
Hence the formulæ of the normal olefins after ethylene, always begin with H_3C, and terminate with $HC:CH_2$; the intermediate terms being CH_2, while the paraffins, after methane, begin and end with H_3C, the intermediate terms being also CH_2.

In the normal olefins, as in the normal paraffins, the carbon atoms form a single chain; but in the iso-olefins there are branches, as in figs. 329, 330.



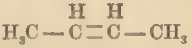
$$\mathrm{{H_3C \atop H_3C}\!>\!C{=}CH_2}$$

Fig. 329.—Iso-butylene.



$$\mathrm{{H_3C \atop H_3C}\!>\!C{=}\underset{H}{\underset{|}{C}}-CH_3}$$

Fig. 330.—Iso-amylene.



$$\mathrm{H_3C-\overset{H}{C}{=}\overset{H}{C}-CH_3}$$

Fig. 331.—Pseudo-butylene.

Iso-butylene is a gas obtained by the action of dehydrating agents on iso-butyl-alcohol.

Pseudo-butylene (fig. 331), another isomeride, is obtained from secondary butyl-alcohol.

A compound metameric with ethylene dichloride is obtained by the action of phosphoric chloride on aldehyd; $H_3C.CO.H + PCl_5 = H_3C.CCl_2.H + POCl_3$. This compound, *ethylidene chloride*, or *dichlorethane*, is evidently formed by the substitution of Cl_2 for the O in aldehyd, so that both chlorine atoms are joined to the same carbon atom, whereas the formation of ethylene chloride by the direct union of ethylene with chlorine, shows that each of the chlorine atoms is combined with a different carbon-atom; $H_2C{=}CH_2 + Cl_2 = \underset{Cl}{\underset{|}{H_2C}}—\underset{Cl}{\underset{|}{CH_2}}$.

Phosphoric chloride is a useful reagent for ascertaining whether an oxygen atom exists as a carbonyl group (CO), or a hydroxyl group (HO); in the former case, it converts the CO group into CCl_2; in the latter, it replaces the HO group by Cl, as when it converts alcohol into ethyl chloride—

$$C_2H_5.OH + PCl_5 = C_2H_5.Cl + HCl + POCl_3.$$

Aldehyd may be regarded as ethylidene oxide $O{=}\underset{H}{C}—CH_3$.

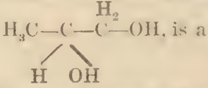
The ethylidene glycol, $(HO)_2{=}\underset{H}{C}—CH_3$, has not been obtained, but *ethyl-ethylidene glycol* $(C_2H_5O)_2{=}\underset{H}{C}—CH_3$, is known as *acetal*, and is obtained by heating alcohol with aldehyd; $2C_2H_5(OH) + O{=}\underset{H}{C}{-}CH_3 = (C_2H_5O)_2{=}\underset{H}{C}{-}CH_3 + H_2O$. Hence the presence of acetal in old wine, and in the last runnings of spirit distilleries. It is made by distilling alcohol with MnO_2 and dilute H_2SO_4, and is a fragrant liquid tasting of nuts, of sp. gr. 0.82, and boiling point 105° C. Oxidising agents convert it into acetic acid. When heated with acetic acid, it yields aldehyd and ethyl acetate.

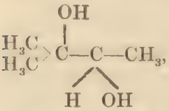
Aldehyd-ammonia (p. 501) may be regarded as $\begin{smallmatrix}HO\\H_2N\end{smallmatrix}{>}\underset{H}{C}{-}CH_3$, or *ethylidene-hydramine*. Chloral hydrate as *trichlorethylidene alcohol;* $(HO)_2{=}\underset{H}{C}{-}CCl_3$.

By careful treatment of ethylene dibromide with potash dissolved in alcohol, it may be converted into *bromethylene*—

$$BrH_2C{-}CH_2Br + KOH = H_2C{=}CHBr + KBr + H_2O.$$

If bromethylene be acted on by zinc-ethide, it is converted into ethyl-ethene, or butylene; $2(H_2C{=}CHBr) + Zn(C_2H_5)_2 = 2(H_2C{=}CH(C_2H_5)) + ZnBr_2$, a mode of formation which justifies the formulæ above assigned to the olefins.

Since glycols contain two HO groups, they may not only be primary, secondary or tertiary, like the alcohols, according to the mode of attachment of the HO; but they may be primary-secondary, or secondary-tertiary, &c., according to the attachment of each of the HO groups. Ethylene glycol, $HO{-}\underset{H_2}{C}{-}\underset{H_2}{C}{-}OH$, is a primary glycol; *propylene glycol*,  $H_3C{-}\underset{H\ \ OH}{C}{-}\overset{H_2}{C}{-}OH$, is a *primary-secondary glycol;* *iso-butylene glycol*, $\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}{>}\underset{OH}{C}{-}\underset{H_2}{C}{-}OH$, is a *primary-tertiary glycol; amylene-glycol*,



$\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}{>}\overset{OH}{C}{-}\underset{H\ \ OH}{C}{-}CH_3$, is a *secondary-tertiary glycol.*

Tertiary glycols are called *pinacones*, and are formed from the ketones by the action of nascent hydrogen; thus, two molecules of acetone, $\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}{>}{=}CO$, combining with 2H, yield *tetra-methyl-pinacone*, or *tetramethyl glycol;* $\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}{>}\underset{OH}{C}{-}\underset{OH}{C}{<}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$

The acids formed by the complete oxidation of the glycols are dibasic acids, because they contain two carboxyle (OC.OH) groups; as in oxalic, $O{=}\overset{HO}{C}{-}\overset{OH}{C}{=}O$, and succinic, $O{=}\overset{HO}{C}{-}\overset{H_2}{C}{-}\overset{H_2}{C}{-}\overset{OH}{C}{=}O$, acids; but those formed by the incomplete oxidation are monobasic, because they contain only one carboxyle group, as in glycolic, $O{=}\overset{H}{C}{-}\overset{OH}{C}{=}O$, and lactic, $H_3C{-}\overset{H}{\underset{OH}{C}}{-}\overset{OH}{C}{=}O$, acids. But they contain a second OH group, which behaves like the hydroxyle in the alcohols, whence they are sometimes called *alcohol-acids*, or *monobasic-diatomic acids*, or *hydroxy-acids*, or simply *oxy-acids*.

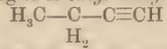
Glycolic acid may be represented as *hydroxyacetic acid*, derived from acetic acid, $\underset{H}{H_2C}.OC.OH$, by the substitution of HO for H, yielding glycolic acid $\underset{OH}{H_2C}.OC.OH$; similarly, lactic acid is *hydroxy-propionic acid*, $H_3C{-}\overset{H}{\underset{OH}{C}}.OC.OH$, derived from propionic acid, $H_3C{-}\overset{H}{\underset{H}{C}}.OC.OH$.

The first member of the series should evidently be hydroxy-formic acid, HO – OC.OH, derived from formic acid, H – OC.OH; but HO.OC.OH would be $O=C\langle^{OH}_{OH}$ (or H_2CO_3), which could not exist because *one atom of carbon cannot hold two hydroxyle groups in stable combination.*

602. *Acetylene hydrocarbons* (see p. 473).—In these, two of the carbon atoms are united by three atom-fixing powers, as in acetylene, H—C≡C—H. They may be prepared from the olefins by combining them with bromine and decomposing the dibromide by distilling with excess of alcoholic potash—

$$BrH_2C—CH_2Br + 2KHO = HC≡CH + 2KBr + H_2O.$$

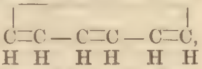
Propylene dibromide, treated in a similar way, yields *methyl-acetylene* or allylene, $H_3C—C≡CH$. The next homologue is *ethyl-acetylene*, or crotonylene—



$$H_3C—\underset{H_2}{C}—C≡CH$$

and so on. The triple linking of the carbon-atoms explains the facility with which acetylene unites directly with other bodies; thus, with bromine, it yields a dibromide, BrHC=CHBr, and a tetrabromide $Br_2HC—CHBr_2$. It also combines with hydrobromic acid, forming ethylidene dibromide; H—C≡C—H + 2HBr = $H_3C—CHBr_2$. It combines with nascent hydrogen, to form ethylene, and with nitrogen (when sparked) to form hydrocyanic acid; HC≡CH + N≡N = 2HC≡N.

When strongly heated, acetylene yields benzene, 3HC≡CH give



$$\overset{|}{\underset{H}{C}}=\underset{H}{C}—\underset{H}{C}=\underset{H}{C}—\underset{H}{C}=\overset{|}{\underset{H}{C}},$$

where the three molecules of acetylene have become singly linked to each other, the third atom-fixing power of each carbon-atom being used for that purpose.

603. In this formula each atom of hydrogen evidently holds the same relative position in the formula, and is therefore of equal chemical value, which accounts for the fact that if any *one* of the atoms be replaced by another radical, the same compound is always formed, whatever the process employed for obtaining it; thus, monochlorobenzene, C_6H_5Cl, has no isomeride, as would be the case if its properties depended upon the particular atom of hydrogen for which the chlorine was substituted. For the same reason there is only one nitrobenzene, $C_6H_5(NO_2)$. In general it may be asserted that *there is only one possible mono-substitution product of benzene* formed by any radical, or that *the mono-substitution derivatives of benzene have no isomerides.*

In order to convey more clearly the idea of the equality in value of the hydrogen atoms in benzene, the formula is often written as a symmetrical plane or solid figure (see p. 723), the commonest representation being that of a regular hexagon formed by closing the extremities of the chain formula given above, leaving each carbon atom at one of the angles. This is known as *Kekulé's benzene ring*, and is represented in fig. 332. Here each atom of carbon is symmetrically situated in relation to the others, having three of its atom-fixing powers attached to adjacent carbon atoms and the fourth attached to hydrogen.

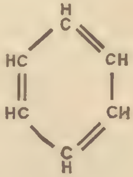
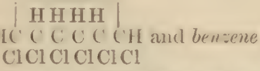


Fig. 332.

In this formula we have evidently an *unsaturated* hydrocarbon, which explains the tendency of benzene (like ethylene) to form *addition*-compounds by direct union with other elements; an example of this is seen in *benzene hexachloride*—



$$C_6H_6Cl_6 \text{ or } \begin{array}{cccccc} | & H & H & H & H & | \\ HC & C & C & C & C & CH \\ Cl & Cl & Cl & Cl & Cl & Cl \end{array} \text{ and } \textit{benzene hexahydride}, C_6H_{12}.$$

Although benzene yields only one mono-substitution product, it is capable of forming three *di-substitution* products, in each of which two atoms of hydrogen are replaced by another radical.

Thus, there are three di-bromobenzenes, all having the formula $C_6H_4Br_2$, and therefore strictly isomeric, and yet having different properties; so there are three di-nitro benzenes, $C_6H_4(NO_2)_2$, and three benzene di-sulphonic acids, $C_6H_4(SO_3H)_2$, and such compounds form perfectly distinct series, so that if they be distinguished as *a*, *b*, and *c* compounds, *a*-di-bromobenzene will yield *a*-di-nitrobenzene, and *a*-benzene-di-sulphonic acid, while *b* and *c* di-bromobenzenes will also yield their proper series of derivatives.

To explain the existence of these three isomeric di-substitution products, it is necessary to assume that different *pairs* of hydrogen atoms in benzene have different chemical values, and that the properties of the di-substitution products depend upon the particular pair of hydrogen atoms replaced by the substituted radical. In order to investigate this it became necessary to *orient* (as it is termed in surveying) the plan of the benzene formula, that is, to mark the situation or *bearing* of its different parts.

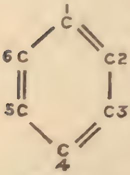


Fig. 333.

604. *Orientation of the benzene ring.*—To effect this, it is necessary to distinguish the carbon atoms, for which purpose they are numbered consecutively as on a watch-face (fig. 333).

The pairs of hydrogen-atoms occupying places 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, 6 and 1, bear the same relation to the figure, and are therefore of equal value, so that whichever pair is replaced by other radicals, the di-substitution products will be identical.

Again, 1 and 3, 2 and 4, 3 and 5, 4 and 6, 5 and 1, 6 and 2, being alternate atoms, bear the same relation to the figure, and their replacement would give rise to identical di-substitution products.

But consecutive atoms, such as 1 and 2, or 2 and 3, have a different relation to the figure from that belonging to alternate atoms, such as 1 and 3, or 2 and 4, so that the replacement of two consecutive atoms of hydrogen would give one kind of derivative (say the *a*-substitution product) and that of two alternate atoms would produce another kind (say the *b*-substitution product).

Lastly, the pairs 1 and 4, 2 and 5, 3 and 6, have the same relation to the figures, and, when replaced by other radicals would give identical products, but these would be different from the *a* and *b* products, and may be called the *c*-substitution products.

As the above lists exhaust all the possible pairs of hydrogen atoms, there can be only three di-substitution derivatives of benzene. Instead of using *a*, *b*, and *c* to distinguish the three isomerides, it is customary to use the prefixes *ortho-*, *meta-*, and *para-*, respectively. When *adjacent* hydrogen atoms in the benzene ring are replaced by other radicals, the product is an *ortho*-compound, when *alternate* hydrogen atoms are replaced, the product is a *meta*-compound. When *opposite* hydrogen atoms are replaced, the product is a *para*-compound. This is sometimes denoted by figures appended to the formula; thus, dibromobenzene (1 : 2) is *ortho-dibromobenzene;* (1 : 3) is *meta-dibromobenzene;* and (1 : 4) is *para-dibromobenzene*, all having the formula $C_6H_4Br_2$.

Ortho- and para-dibromobenzenes are obtained by the action of bromine on benzene; the ortho-compound is a liquid boiling at 224° C. and freezing at −1° C.; the para-compound forms crystals fusing at 89° C., and boiling at 219° C. Meta-dibromobenzene is obtained by the action of ethyl nitrite on meta-dibromaniline—

$$C_6H_3Br_2.NH_2 + C_2H_5.NO_2 = C_6H_4Br_2 + C_2H_4O + N_2 + H_2O.$$

Tri-substitution benzene derivatives.—When three hydrogen atoms in benzene are replaced by other radicals numerous derivatives may be produced. If the same radical is substituted for all three atoms of hydrogen, there may be formed three isomeric substitution-compounds; thus, there are three *tribromobenzenes*, $C_6H_3Br_3$, distinguished as *adjacent* (1 : 2 : 3), fusing at 87° C., *symmetrical* (1 : 3 : 5), fusing at 120° C., and *asymmetrical* (1 : 2 : 4), fusing at 44° C. If the substituted radicals are of two different kinds, say, chlorine and bromine, six isomerides may be formed, and if three different radicals are introduced, say, chlorine, bromine, and NO_2, ten isomerides are possible.

Tetra-substitution derivatives of benzene may also be *adjacent* (1 : 2 : 3 : 4), *symmetrical* (1 : 2 : 4 : 5), and *asymmetrical* (1 : 3 : 4 : 5). With a single substituted radical, only these three isomerides are possible, but two radicals may give 20, three radicals may give 16, and four radicals may give 30 tetra-substitution products. Evidently only one penta-substitution product is possible.

605. *Experimental investigation into the constitution of benzene-derivatives*,—When benzene is acted on by bromine, it yields *bromobenzene* or phenyl bromide, C_6H_5Br, which may have been produced by the substitution of Br for any one of the six H atoms in the benzene ring (fig. 332). Assume that H (1) has been replaced, so that the product may be represented as $C_6Br\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By treating this with nitric acid, the compound $C_6H_4Br(NO_2)$ is produced. Evidently the second H atom which has been replaced by NO_2 is not the same H atom which was replaced by the Br beforehand. Assume that H(2) has been replaced by NO_2, then the nitro-compound will be $C_6Br(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By treating this with nascent hydrogen

(neglecting another reaction) the Br may be removed, and the H whose place it occupied is reinstated, so that nitro-benzene of the formula $C_6\overset{1}{H}(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$ is produced. By treatment with reducing agents (p. 579), this is converted into an amido-substitution derivative (aniline), $C_6\overset{1}{H}(NH_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. When aniline nitrate is acted on by nitrous acid (p. 582) it yields the nitrate of diazobenzene, $C_6\overset{1}{H}(N_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, and by decomposing this with hydrobromic acid, bromobenzene, $C_6\overset{1}{H}(Br)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, is obtained, and this is found to be identical with the bromobenzene produced directly from benzene and bromine, showing that whether H (1) or H (2) is replaced by Br, the same body is produced.

The di-substitution derivatives of benzene may be distinguished by converting them into nitro-compounds.

Ortho-dibromobenzene, $C_6BrBr\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, yields two nitro-substitution products, viz., $C_5BrBr(NO_2)\overset{4}{H}\overset{5}{H}\overset{6}{H}$, and $C_6BrBr\overset{3}{H}(NO_2)\overset{5}{H}\overset{6}{H}$.

Meta-dibromobenzene, $C_6Br\overset{2}{H}Br\overset{4}{H}\overset{5}{H}\overset{6}{H}$, yields three nitro-compounds, viz., $C_6Br(NO_2)Br\overset{4}{H}\overset{5}{H}\overset{6}{H}$, $C_6Br\overset{2}{H}Br(NO_2)\overset{5}{H}\overset{6}{H}$, and $C_6Br\overset{2}{H}Br\overset{4}{H}(NO_2)\overset{6}{H}$.

Para-dibromobenzene, $C_6Br\overset{2}{H}\overset{3}{H}Br\overset{5}{H}\overset{6}{H}$, yields only one nitro-compound—viz., $C_6BrNO_2\overset{3}{H}Br\overset{5}{H}\overset{6}{H}$.

606. *Adjacent* tribromobenzene, $C_6BrBrBr\overset{4}{H}\overset{5}{H}\overset{6}{H}$, can be prepared from either ortho-, $C_6BrBr\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, or meta-dibromobenzene, $C_6Br\overset{2}{H}Br\overset{4}{H}\overset{5}{H}\overset{6}{H}$.

Asymmetrical tribromobenzene, $C_6BrBr\overset{3}{H}Br\overset{5}{H}\overset{6}{H}$, may be prepared from either ortho-, meta-, or para-dibromobenzene, $C_6Br\overset{2}{H}\overset{3}{H}Br\overset{5}{H}\overset{6}{H}$.

Symmetrical tribromobenzene, $C_6Br\overset{2}{H}Br\overset{4}{H}Br\overset{6}{H}$, can only be prepared from meta-dibromobenzene.

The benzene-derivatives, when oxidised, yield three isomeric acids of the formula, $C_6H_4(CO.OH)_2$, which are known as *phthalic*, *isophthalic*, and *terephthalic* acids (*benzene-dicarboxylic acids*). The ortho-derivatives generally yield phthalic acid, $C_6\overset{1}{H}(CO_2H)(CO_2H)\overset{4}{H}\overset{5}{H}\overset{6}{H}$; meta-derivatives generally yield isophthalic acid, $C_6(CO_2H)\overset{2}{H}(CO_2H)\overset{4}{H}\overset{5}{H}\overset{6}{H}$; para-derivatives yield terephthalic acid—

$$C_6(CO_2H)\overset{2}{H}\overset{3}{H}(CO_2H)\overset{5}{H}\overset{6}{H}.$$

607. *Methyl substitution-products of benzene.*—It was shown at p. 477, that toluene, C_7H_8, is methyl-benzene, $C_6H_5.CH_3$, and since it is a mono-substitution derivative, only one toluene is known. Xylene, C_3H_{10}, is dimethyl-benzene, $C_6H_4(CH_3)_2$, and since it is a di-substitution product, there must be three isomeric xylenes. *Orthoxylene*, $C_6(CH_3)(CH_3)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, boils at 141° C. *Metaxylene*, $C_6(CH_3)\overset{2}{H}(CH_3)\overset{4}{H}\overset{5}{H}\overset{6}{H}$, boils at 137° C. *Paraxylene*, $C(CH_3)\overset{2}{H}\overset{3}{H}(CH_3)\overset{5}{H}\overset{6}{H}$, boils at 136° C.

When toluene, $C_6H_5.CH_3$, is acted on by oxidising agents, they convert the CH_3 group into CO.OH, leaving the phenyl (C_6H_5) group untouched, and forming benzoic acid, $C_6H_5.CO.OH$. When xylene, $C_6H_4(CH_3)_2$, is oxidised, the two methyl groups are successively converted into carboxyle, yielding toluic acid $C_6H_4(CH_3)(CO_2H)$, and phthalic acid, $C_6H_4(CO_2H)_2$. The three xylenes yield, respectively, ortho-, meta-, and para-toluic, and ortho-, meta-, and para-phthalic acids.

Ethyl-benzene, $C_6H_5.C_2H_5$, is metameric with the xylenes, but it yields benzoic acid when oxidised. It is prepared by the action of sodium on a mixture of bromobenzene and ethyl-bromide; $C_6H_5Br + C_2H_5Br + Na_2 = C_6H_5.C_2H_5 + 2NaBr$.

When toluene is acted on, in the cold, with chlorine or bromine, the substitution generally takes place in the phenyl group, while, at the boiling point, the methyl group is chiefly acted on.

Thus, in the cold, *mono-*, *di-*, and *tri-chlorotoluene* are formed, $C_6H_4Cl.CH_3$, $C_6H_3Cl_2.CH_3$, and $C_6H_2Cl_3.CH_3$; while, at the boiling-point, *benzyl chloride*, $C_6H_5.CH_2Cl$, *benzylene dichloride*, $C_6H_5.CHCl_2$, and *benzylene trichloride*, $C_6H_5.CCl_3$, are produced. These last yield benzoic acid when oxidised, while the chlorotoluenes yield *mono-*, *di-*, and *tri-chlorobenzoic* acids, $C_6H_4Cl.CO_2H$, $C_6H_3Cl_2.CO_2H$, and $C_6H_2Cl_3.CO_2H$; showing that the chlorine atoms are more firmly held in the phenyl than in the methyl group. Another example of this is furnished by benzylene dichloride, which is converted into benzaldehyd, $C_6H_5.CHO$, by the action of water, while dichlorotoluene, which is metameric with it, is not decomposed by water.

By acting on benzene with a mixture of nitric and sulphuric acids, dinitrobenzene, $C_6H_4(NO_2)_2$, is obtained, and this may be shown to be (chiefly) the meta-compound, by replacing the two NO_2 groups by Br (p. 732), and afterwards by CH_3, when meta-xylene, $C_6(CH_3)\overset{2}{H}(CH)_3\overset{4}{H}\overset{5}{H}\overset{6}{H}$ is obtained; the nitro-compound being *meta-dinitrobenzene*, $C_6(NO_2)\overset{2}{H}(NO_2)\overset{4}{H}\overset{5}{H}\overset{6}{H}$.

608. *Hydroxyl substitution-products of benzene.*—When HO is substituted for H in benzene, a *phenol* is produced; *phenol*, $C_6H_5.OH$, resorcinol, $C_6H_4(OH)_2$, pyrogallol, $C_6H_3(OH)_3$. Benzene is converted into phenol by hydric peroxide—

$$C_6H_6 + HO.OH = C_6H_5.OH + HOH.$$

Resorcinol is *meta-dihydroxybenzene* (1 : 3), and is obtained by fusing meta-benzene-disulphonic acid with potash; $C_6H_4(OH.SO_2)_2 + 2KOH = C_6H_4(OH)_2 + 2\ KOHSO_2$. *Pyrocatechin* is *ortho-dihydroxybenzene*, $C_6H_4(OH)_2$ (1 : 2), and may be obtained by fusing ortho-chlorophenol with potash—

$$C_6H_4Cl(OH)(1:2) + KOH = C_6H_4(OH)_2(1:2) + KCl.$$

Hydroquinone is *para-dihydroxybenzene*, $C_6H_4(OH)_2(1:4)$, and may be obtained by fusing para-iodophenol with potash—

$$C_6H_4I(OH)(1:4) + KOH = C_6H_4(OH)_2(1:4) + KI.$$

Pyrogallol is *meta-trihydroxybeznene*, $C_6H_3(OH)_3(1:2:4)$ (or asymmetric). *Phloroglucol* is *para-trihydroxybenzene*, $C_6H_3(OH)_3(1:3:5)$ (or symmetric).

Cresol is **hydroxytoluene**, $C_6H_4.CH_3.OH$, and since it is a di-substitution derivative of benzene, there are ortho-, para-, and meta-cresols, boiling respectively at 188° C., 201°, and 198°; the first and last are solid. *Orcin* is *para-dihydroxytoluene*, $C_6H_3.CH_3(OH)_2(1:3:5)$.

When the hydroxyl enters the methyl group, instead of the phenyl group, an alcohol is produced, thus, $C_6H_5.CH_2(OH)$ is *benzylalcohol*, which is metameric with cresol.

609. *Naphthalene*, $C_{10}H_8$ (p. 478) is represented by many chemists as $H_4C_4 : C_2 : C_4H_4$, or as containing two benzene rings, *minus* $(CH_2)_2$, as represented in fig. 334.

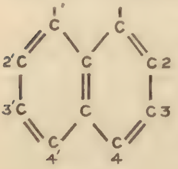
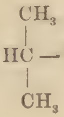
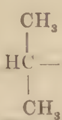
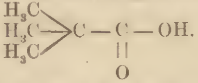


Fig. 334.

On the principles discussed in the case of benzene, such a formula would help to account for the large number of isomeric substitution-products furnished by this hydrocarbon.

610. *Synthesis of the acids of the acetic series.*—It has been shown that acetic acid can be produced synthetically from marsh-gas, carbon dioxide, and water (with the aid of chlorine); the other members of the acetic series of acids can be built up from acetic acid by substituting other radicals for the hydrogen in the methyl group of the formula $H_3C - CO.OH$. The acetic acid is first converted into *acetic ether* (p. 560), $H_3C - CO.OC_2H_5$. This is treated with sodium and converted into *sodacetic ether* (p. 560), $Na\overset{H}{\underset{H}{C}} - CO.OC_2H_5$. By digesting this for several hours, in a sealed tube at 100° C. with methyl iodide, its sodium is replaced by methyl, and methyl acetic ether, $H_3C - \overset{H}{\underset{H}{C}} - CO.OC_2H_5$ is obtained. This is identical with propionic ether $H_5C_2 - CO.OC_2H_5$, and by saponifying it with potash, and distillation with sulphuric acid, propionic acid, $H_5C_2 - CO.OH$, is obtained.

If the sodacetic acid be digested with ethyl-iodide, it yields *ethyl-acetic ether*, $H_5C_2 - \overset{H}{\underset{H}{C}} - CO.OC_2H_5$, which is butyric ether, and from this, butyric acid is easily prepared. When di-sodacetic ether, $H\overset{Na}{\underset{Na}{C}} - CO.OC_2H_5$, is decomposed by methyliodide, di-methyl-acetic ether,  $HC(CH_3)(CH_3)—CO.OC_2H_5$, is obtained, which yields di-methyl acetic acid,  $HC(CH_3)(CH_3)—CO.OH$, or isobutyric acid (p. 728). This reaction shows that butyl, C_4H_9, is $CH_2(CH_2.C_2H_5)$, or *ethylo-methyl-methyle*, while iso-butyl, C_4H_9, is $CH_2.CH(CH_3)_2$, or *di-methylo-methyl-methyle*.

Di-sodacetic ether, with ethyl iodide, yields *di-ethyl-acetic ether*, from which di-ethyl acetic acid or *iso-caproic acid* is obtained. Amyl iodide and sodacetic ether yield *amyl acetic* or capric ether. *Tri-sodacetic ether*, $Na_3C.CO.OC_2H_5$, reacts with methyl-iodide, to form trimethyl acetic ether, $(CH_3)_3C.CO.OC_2H_5$, which yields *trimethyl acetic* or tertiary valeric acid,  $(H_3C)_3{>}C—C(=O)—OH$.

611. *Constitution of uric acid.*—Uric acid has been obtained synthetically by heating glycocine (p. 673) with an excess of urea to a high temperature in a sealed tube; glycocine being amido-acetic acid, its formula is $CH_2(NH_2).CO.OH$, and its reaction with three molecules of urea $3CO(NH_2)_2$, yields uric acid, $C_5H_4N_4O_3$, together with $3NH_3$ and $2H_2O$. This indicates the existence in uric acid of at least two groups, one containing C united to O, and the other containing N united to H.

When uric acid is oxidised by nitric acid, it gives rise to a large number of products, many of which are connected with urea, and contain a radical with three carbon atoms, such as *alloxan* or *mesoxalyl urea*, $CO.N_2H_2(C_3O_3)''$, *dialuric acid* or *tartronyl urea*, $CO.N_2H_2(C_3H_2O_3)''$, *parabanic acid* or *oxalyl urea*, $CO.N_2H_2(C_2O_2)''$, and *barbituric acid* or *malonyl urea*, $CO.N_2H_2(C_3H_2O_2)''$. It would appear therefore that there must be three carbon-atoms directly united, and one group containing C, O, N and H which is easily converted into urea and its derivatives. These conditions would be fulfilled by the formula $OC.C_2(CON_2H_2)_2$, resolvable into $(CO)_3(CN_2NH_2)_2$, or by the structural formula shown in fig. 335.

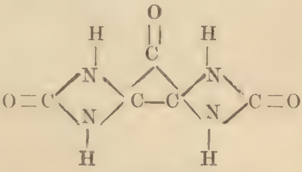


Fig. 335.—Uric acid.

612. In investigating the chemical structure of the molecules of organic bodies, much assistance is derived from the observation of their physical properties, among which the following are the most important:—

(1) The *fusing point* of a solid, the *boiling point* of a liquid, and the *specific gravity* of a vapour.

(2) The *specific volume* of a liquid, obtained by dividing its molecular weight by its specific gravity (calculated for the temperature at which the liquid boils).

(3) The *optical properties* of a liquid, or of a solid body in solution; especially the *action on polarised light*, the *refractive power*, the *absorption spectrum*, and the *magnetic rotatory power* deduced from its action on a ray of polarised light when under the influence of magnetism.

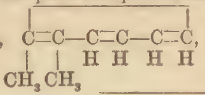
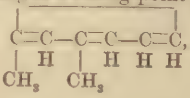
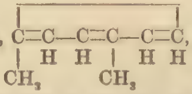
613. Fusing points of organic compounds.—In order that a solid may fuse, it must first attain to a degree of temperature, called the *fusing point* of the solid, and must then have a certain amount of motion imparted to its molecules by the tranformation (into motion) of an amount of heat which is termed *latent heat* or *heat of fusion*. This motion enables the molecules to circulate more or less freely among themselves, and to extend themselves in a horizontal plane.

The fusing point, as indicated by the thermometer, therefore, is the temperature at which the molecules become capable of converting the heat subsequently acquired into the motion proper to the liquid condition. This temperature will depend upon the constitution of the molecules, which regulates their relation to adjacent molecules.

If the *cohesion* which limits the motion of molecules in a solid mass be similar in character to the *gravitation* which limits the motion of masses of matter, it will be greater among those molecules which have the larger *mass*, that is, the highest molecular weight, and these should have the highest fusing points, since a larger amount of progressive motion (or *temperature*) must be imparted to them to render them capable of acquiring the freedom of motion proper to the liquid condition. But it is by no means true that the fusing-point is always higher when the molecular weight is greater; for palmitin, with a molecular weight of 806, fuses at 63° C., while urea, with a molecular weight of 60, fuses at 130° C. It may be stated, however, that, in the case of homologous series, the fusing-point generally rises as the molecular weight increases; thus the paraffin and olefin hydrocarbons are liquids until they contain sixteen atoms of carbon. The substitution of HO for H tends to raise the fusing-point, so that the paraffin alcohols containing more than seven carbon atoms are solids, and this is also the case with the aldehyds.

The acids derived from the paraffins exhibit remarkable anomalies; the fusing point of acetic acid, $CH_3.CO_2H$, being 17° C.; that of butyric, $CH_3(CH_2)_2.CO_2H$, 0° C.; valeric, $CH_3(CH_2)_3.CO_2H$, below $-16°$ C.; caproic, $CH_3(CH_2)_4.CO_2H$, $-2°$ C.; heptylic, $CH_3(CH_2)_5.CO_2H$, $-10°.5$ C.; while caprylic acid, $CH_3(CH_2)_6.CO_2H$, fuses at about 16° C.; after this, the fusing points of the acids rise for each addition of CH_2, but in a diminishing ratio, so that whilst the fusing point of capric acid, $CH_3(CH_2)_8.CO_2H$, is about 14° higher than that of caprylic, the fusing point of stearic acid, $CH_3(CH_2)_{16}.CO_2H$, is only 7° above that of palmitic, $CH_3(CH_2)_{14}.CO_2H$.

In the case of the metameric paraffin derivatives, the fusing point is generally higher in those compounds which contain most carbon in the form of CH_3; thus, pseudo-valeric or tertiary valeric acid, $C(CH_3)_3.CO_2H$, fuses at about 34° C., while normal valeric acid, $CH_3(CH_2)_3.CO_2H$, fuses below $-16°$ C. Again, tertiary butyl-alcohol, $C(CH_3)_3.OH$, fuses at 25° C.; and normal butyl-alcohol, $CH_3(CH_2)_3.OH$, is liquid even below 0° C.

In the benzene-hydrocarbons, the substitution of CH_3 for H raises the fusing point; thus, toluene, $C_6H_5.CH_3$, and xylene, $C_6H_4(CH_3)_2$, are liquids; but durene, $C_6H_2(CH_3)_4$, fuses at 80° C. In these also, when they have the same molecular weight, the fusing point rises with the number of methyl groups directly united to carbon; for example, amyl-toluene, $C_7H_7.CH_3(CH_2)_4$, is liquid, while hexamethyl-benzene, $C_6(CH_3)_6$, is solid, fusing at 150° C. Even in compounds which are strictly isomeric, the position of the component radicals will affect the fusing point, the para-compound having generally the highest fusing-point; thus, ortho-xylene,  $\underset{CH_3}{C}{=}\underset{CH_3}{C}-\underset{H}{C}{=}\underset{H}{C}-\underset{H}{C}{=}\underset{H}{C}$, and meta-xylene,  $\underset{CH_3}{C}{=}\underset{H}{C}-\underset{CH_3}{C}{=}\underset{H}{C}-\underset{H}{C}{=}\underset{H}{C}$, are liquids; but para-xylene,  $\underset{CH_3}{C}{=}\underset{H}{C}-\underset{H}{C}{=}\underset{CH_3}{C}-\underset{H}{C}{=}\underset{H}{C}$, is a solid, fusing at 15° C.

614. Boiling points of organic compounds.—The boiling point of a liquid is that temperature at which its molecules are capable of converting heat into motion sufficient to enable them to overcome entirely the attraction holding them to each other, and to extend themselves in all directions through space. Under ordinary conditions, their extension is impeded by the pressure of the atmosphere upon the surface of the liquid, so that, for experimental work, the boiling point is that temperature at which the molecules are capable of acquiring sufficient motion to overcome a pressure of 760 millimetres of mercury (at 0° C.). Since the boiling point refers to a certain standard of external work, it exhibits a more definite relation to the constitution of the molecules than is the case with the fusing point. In homologous series, the boiling-point increases with the molecular weight, but the increase due to each addition of CH_2 varies in different series. It is most uniform in the normal primary alcohols of the paraffin series (p. 490), where each addition of CH_2 increases the boiling point, on the average, by 19°.4 C. In the series of aldehyds derived from these alcohols (p. 502), the increase in boiling point is also fairly regular, but it averages 26°.2 for each addition of CH_2. In the corresponding acids, the increase is much less uniform, but the average increase is about 19°. In the single ketones (p. 456), the mean increase in boiling point for each CH_2 added is 20°.5. In the simple ethers, the increase is 26°.

In the homologous series of hydrocarbons, the increase in boiling point for each addition of CH_2 is irregular, but generally diminishes as the number of carbon-atoms increases. Those hydrocarbons of the paraffin and olefin series which contain the same number of carbon-atoms exhibit a similarity in their boiling points:—

Paraffins	C_5H_{12}	38°	C_6H_{14}	70°	C_7H_{16}	98°	C_8H_{18}	125°	$C_{16}H_{34}$	278°
Olefins .	C_5H_{10}	35°	C_6H_{12}	70°	C_7H_{14}	100°	C_8H_{16}	125°	$C_{16}H_{32}$	275°

The isologous hydrocarbons of the acetylene series have higher boiling points, and those of the benzenes are higher still—

Acetylenes	C_5H_8	45°	C_6H_{10}	80°	C_7H_{12}	107°	C_8H_{14}	133°	$C_{10}H_{18}$	165°
Benzenes	...		C_6H_6	81°	C_7H_8	111°	C_8H_{10}	140°	$C_{10}H_{14}$	190°

The substitution of HO for H in the conversion of the paraffin hydrocarbons into alcohols increases the boiling point greatly, but in a ratio which decreases in nearly the same proportion in which the molecular weight of the alcohol increases—

Hydrocarbons	C_5H_{12}	38°	C_6H_{14}	70°	C_7H_{16}	98°	C_8H_{18}	125°
Alcohols .	$C_5H_{12}O$	137°	$C_6H_{14}O$	157°	$C_7H_{16}O$	170°	$C_8H_{18}O$	191°

A similar increase in boiling point is produced by the substitution of HO for H in the conversion of an aldehyd into an acid—

Aldehyds .	C_2H_4O	20.8	C_3H_6O	49°	C_4H_8O	75°	$C_5H_{10}O$	102
Acids .	$C_2H_4O_2$	118°	$C_3H_6O_2$	142°	$C_4H_8O_2$	163°	$C_5H_{10}O_2$	175°

Metameric bodies which belong to the same class often have nearly the same boiling points—

Propione	$C_2H_5.CO.C_2H_5$	100°
Methyl-propyl ketone	$CH_3.CO.C_3H_7$	101°
Methyl-butyl ketone	$CH_3.CO.C_4H_9$	127°
Propyl-ethyl ketone	$C_3H_7.CO.C_2H_5$	128°
Ethyl formate	$C_2H_5.CHO_2$	55°
Methyl acetate	$CH_3.C_2H_3O_2$	56°

But this is not the case when they belong to different classes—

Methyl-ethyl ketone	$CH_3.CO.C_2H_5$	81°
Methyl-allyl ether	$CH_3.O.C_3H_5$	46°
Propione	$C_2H_5.CO.C_2H_5$	100°
Ethyl-allyl ether	$C_2H_5.O.C_3H_5$	64°

The ethereal salts have lower boiling points than the acids which are metameric with them—

Methyl formate	$CH_3.CHO_2$	36°
Ethyl formate	$C_2H_5.CHO_2$	55°
Acetic acid	$H.C_2H_3O_2$	118°
Propylic acid	$H.C_3H_5O_2$	142°

In the isomeric hydrocarbons, the normal compound has the highest boiling point, which falls as the number of methyl groups increases; thus, normal butane, $H_3C(CH_2)_2CH_3$, is liquefied at 1° C., while iso-butane, $H_3C.CH(CH_3).CH_3$, remains liquid till – 17° C.

		B.P.
Pentanes, C_5H_{12}.		
Normal	$H_3C(CH_2)_3CH_3$	38°
Iso-	$H_3C.CH_2.CH(CH_3).CH_3$	30°
Neo-	$(H_3C)_2C(CH_3)_2$	9.5°
Hexanes, C_6H_{14}.		
Normal	$H_3C(CH_2)_4CH_3$	72°
Iso-	$H_3C(CH_2)_2CH(CH_3)_2$	62°
Neo-	$(H_3C)_2(CH)_2(CH_3)_2$	58°
Tri-methyl-ethyl methane	$(H_3C)_3C(C_2H_5)$	45°
Heptanes, C_7H_{16}.		
Normal	$H_3C(CH_2)_5CH_3$	97°
Iso-	$H_3C(CH_2)_3CH(CH_3)_2$	91°
Tri-ethyl methane	$(CH_2.CH_3)_3CH$	96°
Di-ethyl-di-methyl methane.	$(CH_2.CH_3)_2C(CH_3)_2$	86°

It is evident that the boiling point is lowered, in these isomeric hydrocarbons, by the substitution of ethyl and methyl for hydrogen, and is lowest in those compounds in which the carbon is united to the compound radicals only. The same tendency is observed in the isomeric olefins; thus—

Amylene . . . $H_3C(CH_2)_2CH : CH_2$, boils at 73°, and
Iso-amylene . . $(H_3C)_2C : CH(CH_3)$ „ 35°

Isomeric alcohols.—The normal primary alcohols have the highest boiling points, then come the iso-alcohols, while the secondary and tertiary alcohols have the lowest boiling points.

		B.P.
Propyl alcohols, $C_3H_7.OH$.		
Normal primary	$H_3C.CH_2.CH_2.OH$	97°
Iso-	$(H_3C)_2.CH.OH$	84°
Butyl alcohols, $C_4H_9.OH$.		
Normal primary	$H_3C(CH_2)_2CH_2.OH$	117°
Iso-	$(H_3C)_2CH.CH_2.OH$	106°
Secondary	$H_3C.CH_2.CH(OH)CH_3$	97°
Tertiary iso-	$H_3C.C(CH_3)_2.OH$	83°
Amyl alcohols, $C_5H_{11}.OH$.		
Normal primary	$H_3C(CH_2)_3CH_2.OH$	137°
α-Iso-	$(H_3C)_2CH.CH_2.CH_2.OH$	129°
β-	$H_3C.CH_2.OH.CH.CH_2CH_3$	127°
α-Secondary	$H_3C(CH_2)_2.CH(OH).CH_3$	121°
β-	$H_3C.CH_2.CH(OH).CH_2.CH_3$	116°
Secondary iso-	$(H_3C)_2CH.CH(OH)CH_3$	106°
Tertiary iso-	$H_3C.CH_2.C(CH_3)_2.OH$	100°
Hexyl alcohols, $C_6H_{13}.OH$.		
Normal primary	$H_3C(CH_2)_4CH_2.OH$	157°
α-Secondary	$H_3C(CH_2)_3CH(OH).CH_3$	137°
Diethyl-methyl carbinol	$(C_2H_5)_2.C(OH)CH_3$	120°
Pinacolyl alcohol	$(H_3C)_3.C.CH(OH)CH_3$	120°
Dimethyl-propyl carbinol	$(H_3C)_2.C(OH)(CH_2)_2.CH_3$	115°
Dimethyl-isopropyl carbinol	$(H_3C)_2.C(OH)CH(CH_3)_2$	113°

Isomeric aldehyds.—Here, also, the normal compounds have the highest boiling points.

		B.P.
Butyric aldehyds, $C_3H_7.CHO$.		
Normal	$H_3C(CH_2)_2.CHO$	75°
Iso-	$(H_3C)_2CH.CHO$	61°
Valeric aldehyds, $C_4H_9.CHO$.		
Normal	$H_3C(CH_2)_3CHO$	102°
Iso-	$(H_3C)_2CH.CH_2.CHO$	92°.5

Isomeric Acids.—These exhibit a similar relation in their boiling points.

		B.P.
Butyric acids, $C_3H_7.CO_2H$.		
Normal	$H_3C(CH_2)_2.CO_2H$	163°
Iso-	$(H_3C)_2CH.CO_2H$	154°
Valeric acids, $C_4H_9.CO_2H$.		
Normal	$H_3C(CH_2)_3.CO_2H$	184°
Iso-	$(H_3C)_2CH.CH_2.CO_2H$	175°
Methyl-ethyl-acetic acid	$H_3C.CH_2.CH(CH_3).CO_2H$	173°
Trimethyl-acetic acid	$(H_3C)_3.C.CO_2H$	161°
Crotonic acids, $C_3H_5.CO_2H$.		
Crotonic	$H_3C.CH : CH.CO_2H$	182°
Iso-	$H_2C : CH.CH_2.CO_2H$	172°

615. *Influence of position-isomerism on the boiling point.*—When any other element or group is substituted for hydrogen in an organic compound, the boiling point is raised, and if more than one atom of hydrogen be replaced, the boiling point, in the isomerides thus produced, will generally be higher where the substituting radicals are at the greatest distance from each other. Thus, ethylidene dichloride, $H_3C.CHCl_2$, boils at 58°; whilst ethene dichloride, $ClH_2C.CH_2Cl$, does not boil till 85°. Again, dibromopropane, $H_3C.CBr_2.CH_3$, boils at 114°; propene dibromide, $H_3C.CHBr.CH_2Br$, at 142°; and trimethene dibromide, $BrH_2C.CH_2.CH_2Br$, at above 160°. Ortho-cresol, $C_6H_4.CH_3.OH(1:2)$, boils at 190°; meta-cresol (1 : 3) at 195°;

and para-cresol (1 : 4) at 198°. Ortho-chloraniline, $C_6H_4Cl.NH_2$(1 : 2), boils at 207°; meta-chloraniline (1 : 3) at 230°; and para-chloraniline (1 : 4) at 231°. Diamidotoluene, $C_6H_3(CH_3)(NH_2)_2$(1 : 2 : 3), boils at 270°; and (1 : 2 : 4) at 280°. Further investigation of the boiling points of isomerides is necessary fully to establish this law.

616. Specific volumes of organic liquids.—It has been seen that the specific volumes of the *vapours* of organic compounds, obtained by dividing the molecular weight by the vapour-density, are in all cases alike; but this is not the case with the specific volumes of *liquids*, which depend upon the attraction exerted between their molecules, which must of course vary with the nature of the molecules themselves. Since, at their respective boiling points, all liquids are in a similar condition in regard to the further effect of heat upon them, it might be expected that their molecular weights, divided by their specific gravities (at the boiling point) would yield quotients bearing some definite relation to each other, since these quotients represent the *molecular volumes* of the compounds in the liquid state (at the boiling point); that is, the relative (or specific) volumes, within which the motions of each molecule are restricted, or the space which each molecule keeps free from other molecules.

The molecular volume of water, calculated in this way, is 18.8; that of methyl-alcohol is 42. Then $CH_4O - H_2O = CH_2$; and $42 - 18.8 = 23.2$, which is the increase in molecular volume, due to the addition of CH_2 to H_2O. The molecular volume of ethyl-alcohol is 62.5, or higher than that of methyl-alcohol by 20.5, which represents the increase due to CH_2. The molecular volume of acetic acid is 64, and that of formic acid 42, giving 22 as the increase due to CH_2. The mean of the three values is 21.9, and this is almost exactly the difference in the molecular volumes calculated for the homologous acids, from formic to valeric. The molecular volume appears to depend upon the number and nature of the atoms contained in the molecule, rather than upon their grouping; thus, ethyl-acetate, $C_2H_5.C_2H_3O_2$, has the same molecular volume as its metameride, butyric acid, $HO.C_4H_7O$. Octane, C_8H_{18}, has a molecular volume = 187, and if we deduct from this $(CH_2)_8 = 176$, the difference, 11, represents the molecular volume of H_2, giving 5.5 for the *atomic volume* of hydrogen. Cymene, $C_{10}H_{14}$, has the molecular volume 187, which differs from $(CH_2)_7$, or 22×7, by 33, which represents the increase in molecular volume due to C_3, and gives 11 for the atomic volume of carbon.

By deducting the volume of H_2 (11) from that of H_2O (18.8), 7.8 is obtained for the atomic volume of oxygen.

From these values the specific volumes of many molecules may be calculated, and are found to agree very nearly with those obtained by dividing the molecular weight by the specific gravity of the liquid at its boiling-point; for example—

Methyl alcohol, CH_4O, gives $11 + (5.5 \times 4) + 7.8 = 40.8$ instead of 42
Ethyl ,, C_2H_6O ,, $(11 \times 2) + (5.5 \times 6) + 7.8 = 62.8$,, 62.5
Ether ,, $C_4H_{10}O$,, $(11 \times 4) + (5.5 \times 10) + 7.8 = 106.8$, which is correct.
Phenol ,, C_6H_6O ,, $(11 \times 6) + (5.5 \times 6) + 7.8 = 106.8$,, ,,

But formic acid, CH_2O_2, the specific volume of which is 41.5, gives only 37.6 as the sum of $11 + (5.5 \times 2) + (7.8 \times 2)$.

Again, acetone, C_3H_6O, with a specific volume = 77.6, gives only 73.8 (which agrees with that found for allyl-alcohol, also C_3H_6O) by the addition of

$$(11 \times 3) + (5.5 \times 6) + 7.8.$$

The structural formula of acetone is $H_3C—\overset{\overset{O}{||}}{C}—CH_3$, the oxygen being doubly ked to a carbon atom, whilst in the alcohols, ethers and phenols, it is only singly linked to a carbon atom.

Deducting from the specific volume of acetone (77.6) that of C_3H_6 (66), there remains 11.6 as the atomic volume of oxygen, when doubly linked to a carbon-atom.

Formic acid has the structural formula, $H\overset{\overset{O}{||}}{C}—OH$, so that it contains a singly linked and a doubly linked oxygen atom; hence its molecular volume should be the sum of $11 + (5.5 \times 2) + 7.8 + 11.6 = 41.4$, which is very nearly correct.

Acetic acid, $H_3C(C:O)OH$, gives $(5.5 \times 4) + (11 \times 2) + 7.8 + 11.6 = 63.4$, instead of 63.6.

Aldehyd, $H_3C(C:O)H$, gives $22+22+11.6=55.6$, instead of 56.5, whereas if its formula were $H_2C.O.CH_2$, it would give $22+22+7.8=51.8$.

The specific volume of an atom of nitrogen singly linked to carbon, as in methylamine, $H_3C—NH_2$, is 2.3; but when trebly linked to carbon, as in methyl cyanide, $H_3C—C\equiv N$, its specific volume is 17.

Sulphur, singly linked to carbon, has the specific volume 23; but when doubly linked, it is 28.6. The specific volume of chlorine is 22.8, of bromine 27.8, and of iodine 37.5.

Recent experiments indicate many exceptions to the simple laws of specific volume here set forth. Thus, ethylene chloride, $ClH_2C.CH_2Cl$, and ethylidene chloride, $H_3C.CHCl_2$, which have the calculated specific volume, 89.5, give, by experiment, respectively, 85.34 and 88.96, a difference too great to be ascribed to experimental errors. Benzene, and some other members of the aromatic group, also exhibit considerable deviation, the observed specific volumes being lower than those calculated.

617. OPTICAL PROPERTIES OF ORGANIC COMPOUNDS.—Since the phenomena of light depend upon the waves excited in the æther which fills the spaces between the molecules of matter, the motions of these molecules must exert an influence upon the optical properties of the substances which they compose.

The molecular conditions which regulate the *colour* of compounds, by enabling them to absorb certain of the waves composing white light, and to reflect or transmit others, are not as yet understood, but colour is most commonly associated with high molecular weight.

Much attention has been devoted to the comparison of the *refractive powers* of liquid organic compounds, that is, to the amount of deviation from its original path which a wave of light suffers in passing through the liquid in any direction except that perpendicular to the surface. The full discussion of this subject requires the study of optics, but it may be stated that from the amount of deviation is calculated the *specific refractive power* of the liquid, which is closely connected with the nature of its molecules. The *molecular refractive energy*, or *refraction-equivalent*, is found by multiplying the molecular weight by the specific refractive power. Compounds which have the same molecular weight and belong to the same or to nearly related classes of organic compounds generally, have nearly the same refraction equivalent; thus, the number for methyl acetate, $CH_3.C_2H_3O_2$ is 28.78, and that for ethyl formate, $C_2H_5.CHO_2$ is 28.61. Butyl-alcohol, $C_4H_9.OH$, gives 36.11, and ether, $C_2H_5.O.C_2H_5$, 36.26. Polymeric bodies have refraction equivalents nearly proportionate to their molecular weights; thus, aldehyd, C_2H_4O, has the refraction equivalent 18.5, butyric acid, $C_4H_8O_2$, 36.6, and paraldehyd, $C_6H_{12}O_3$, 52.5. In the homologous alcohols and acids derived from the paraffin hydrocarbons, the refraction-equivalent increases by about 7.6 for each addition of CH_2; thus, acetic acid, $C_2H_4O_2$, having the refraction-equivalent 21.1, œnanthic acid should give $21.11+(7.6\times5)=59.1$, which nearly agrees with that observed, 59.4.

By a method similar to that explained in the case of specific volumes, the refraction-equivalents of the elements may be calculated, and they are found to be, for carbon, 4.86, for hydrogen, 1.29, for oxygen singly linked to carbon, 2.71, and for oxygen doubly linked, 3.29. From these numbers, the refraction-equivalent of a liquid may be calculated from its formula, as in the case of its specific volume, and the result agrees very nearly, in a great many cases, with that obtained by experiment. But there is sufficient deviation to indicate that the grouping of the atoms, as well as their nature and number, influences the refraction-equivalent. Thus, in the terpenes, the observed equivalent exceeds that calculated by the constant number 3, while in the benzenes the excess amounts to 6. It would appear that when a carbon atom is doubly linked to another carbon atom, its refraction-equivalent is 5.86 instead of 4.86, so that the six doubly linked carbon atoms in the benzene ring (page 731) would explain the excess in the refraction-equivalent.

When liquids having different refraction-equivalents are mixed, the refraction-equivalent of the mixture is the sum of those of its constituents, so that the proportions in which these are present may be calculated.

Polarised light, in which the æther waves all vibrate in the same plane, undergoes a change in its passage through some liquids, the plane of vibration being turned through a certain angle towards the right or left, so that an *analyser* or transparent crystal, through which the original polarised light failed to pass, has now to be rotated through a certain number of degrees to the right or left, in order again to become opaque to the polarised beam. The angle through which the analyser must be turned to effect this is called the *angle of rotation*, and the liquid under examination is said to be *dextro-* (+) or laevo-(−) rotatory accordingly as it is necessary to turn the analyser round in the direction of the hands of a watch or otherwise. This angle of rotation, in the case of any given substance, varies directly as the strength of the solution, its specific gravity, and the length of the column of liquid through which the light passes. For different substances, the angle of rotation also varies with the *specific rotatory power*, which is found by dividing the angle of rotation by the product obtained by multiplying together the weight of the substance in one gramme of the liquid, the specific gravity of the liquid, and the length of the column in decimetres. For example, a beam of polarised light was passed through a tube with glass ends, .50 decimetre long, filled with turpentine, of specific gravity (at the temperature of the experiment) .8712, and it was requisite to turn the analyser 16° in the opposite direction to the hands of a watch in order to prevent light from reaching the eye of the observer. This would give for the specific (laevo) rotatory power, $\frac{16}{1 \times .8712 \times .5} = 36.7$. It is evident that if the specific rotatory power of a substance be known, a calculation like this would give the weight contained in each gramme of the solution, and this is turned to account in the *saccharimeter* for determining the proportion of sugar in a solution.

This rotatory power is found most commonly in vegetable and animal products and their immediate derivatives, as will have been seen in the description of such bodies, and it has been pointed out that it depends upon some peculiarity in the structure of the molecule. Recent observations render it probable that much information will be derived from the study of circular polarisation with respect to the true configuration of molecules.

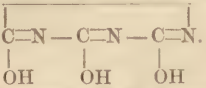
All liquids exhibit some rotatory power for polarised light when they are under the influence of a powerful (electro) magnet, and the amount of the rotation, compared with that produced by water under the same conditions is called the *magnetic rotatory power*. The *molecular magnetic rotation* obtained by mutiplying the rotatory power by the molecular weight, and dividing by the specific gravity of the liquid, exhibits a definite relation to the composition of the molecule, and increases by 1.023 for each addition of CH_2 in homologous series. Proceeding on the same principle as in the case of specific volumes (page 739), the *atomic magnetic rotatory power* of carbon is found to be .515, that of hydrogen, .254, of singly linked oxygen, .194, and of doubly linked oxygen, .263, and from these, in many cases, the molecular magnetic rotatory power of compounds may be calculated, or conversely, a knowledge of the rotatory power may be applied to determine a molecular formula.

618. *Absorption spectra of organic compounds for chemical rays.*—The light emanating from the sun and from the electric spark is accompanied by many other waves whose period of vibration is so short that they produce no impression upon the eye, or upon the thermometer, and are only detected by their power of chemically decomposing the salts of silver and other photographic materials. The shortness of these waves causes them to suffer a greater amount of deviation or refraction than the luminous waves when the light is passed through a prism, so that their effects are chiefly perceived in that part of the spectrum which lies beyond the violet light, and is usually termed the *ultra-violet*. Many substances which are perfectly transparent are able to intercept a large proportion of these *actinic* waves as they are termed, and are said to be *adiactinic*, whilst those which transmit them freely are *diactinic*.

Rock crystal, or quartz, is much more diactinic than glass, and lenses and prisms of this material are used in experiments upon this subject, the light of a stream of electric sparks being allowed to pass through the slit of a spectroscope (page 273), through a cell with quartz sides containing the liquid under examination, then through a quartz lens and prism, and afterwards upon a sensitive photographic plate upon which that portion of the ultra-violet waves which has passed through leaves its impression.

It has been shown, by such experiments, that the normal alcohols derived from the paraffins are highly diactinic, and that the corresponding acids are somewhat less so, absorbing more of the highly refrangible waves remote from the violet end of the spectrum; the diactinic character decreasing, in both acids and alcohols, as the molecular weight increases. Benzene and its derivatives are highly adiactinic, and, when employed in strong solutions, are often capable of absorbing all the ultra-violet waves; but when diluted to a certain extent with water or alcohol, they allow some of the waves to pass, and produce photographs of spectra exhibiting *absorption bands* due to this *selective absorption*. Since isomeric benzene derivatives exhibit very different absorption-bands, the selective absorption must be due to vibrations within the molecules, while the general absorption, which varies with the molecular weight, is caused by the vibration of the molecules themselves. There is very strong evidence that the absorption-bands in the ultra-violet spectrum are exhibited only by those compounds in which the carbon-atoms form *closed chains*, as in benzene (page 731), and naphthalene (page 734), in which there are three pairs of doubly linked carbon atoms.

Hydrocyanic acid is remarkably diactinic, and gives no absorption-bands, but cyanuric acid exhibits strong absorption-bands, and those compounds in which an atom of nitrogen has been substituted for an atom of carbon in the benzene or naphthalene nucleus, as in pyridine, C_5H_5N, and quinoline, C_9H_7N, still retain the property of selective absorption for the ultra-violet rays. Probably cyanuric acid contains a closed chain with three carbon-atoms doubly linked to nitrogen: thus,



$$\underset{\mathrm{OH}}{\mathrm{C}}{=}\mathrm{N}-\underset{\mathrm{OH}}{\mathrm{C}}{=}\mathrm{N}-\underset{\mathrm{OH}}{\mathrm{C}}{=}\mathrm{N}.$$

The terpenes, $C_{10}H_{16}$, possess, in a high degree, the power of absorbing the ultra-violet rays, though they are inferior in this respect to benzene and its derivatives. Terpenes of the formula, $C_{15}H_{24}$, have a greatly increased absorption power, but neither the terpenes themselves nor their oxides or hydrates exhibit absorption-bands if they are pure, but if they contain benzene derivatives they exhibit absorption-bands when diluted with alcohol, thus affording a delicate test for adulteration.

Starch, glucose, saccharose, diastase, and gelatin are highly diactinic, and show no absorption-bands, while albumen, casein, and serin exhibit absorption-bands in dilute solutions.

The photographic absorption-spectra afford a most accurate method of identifying organic substances, and a most delicate test of their purity, since the absorption-bands are visible in solutions of extreme dilution.

Hartley infers, from the wave-lengths of the absorbed rays, that the molecule of benzene has 1248 billions of vibrations per second, that of naphthalene 1177 billions, and that of anthracene 910 billions.

*** *In consequence of the change in the classification adopted in the Fifth Edition, the following alcohol-derivatives have been omitted from their proper places.*

Chloral, or *trichloraldehyd*, $CCl_3.COH$, is prepared by passing thoroughly dried chlorine into absolute alcohol, which must be placed in a vessel surrounded by cold water at the commencement, because the absorption of chlorine is attended by great evolution of heat. The passage of chlorine is continued for many hours, and when the absorption takes place slowly, the alcohol is gradually heated to boiling, the chlorine being still passed in until the liquid refuses to absorb it. The principal reaction is represented by the equation, $CH_3.CH_2.OH + 4Cl_2 = 5HCl + CCl_3.COH$; but the HCl acts upon part of the alcohol, forming ethyl chloride and water. On cooling, the product solidifies to a crystalline mixture of the compounds of water and alcohol with chloral, from which the latter may be obtained by distillation with sulphuric acid.

On the large scale, chlorine is passed into alcohol of at least 96 per cent. for twelve or fourteen days. The crude product is heated with an equal weight of strong sulphuric acid in a copper vessel lined with lead. HCl escapes at first, and the chloral distils over at about 100° C. The distillate is rectified, and mixed with water in glass flasks, when *chloral hydrate*, $CCl_3.COH.H_2O$, is formed, which is poured into porcelain basins, where it crystallises.

Chloral is a liquid of sp. gr. 1.5, and boiling point, 97° C. It has a pungent tear-exciting odour, and irritates the skin. Exposed to air, it absorbs water and forms crystals of the hydrate, which is produced at once when chloral is stirred with a few drops of water, heat being evolved. When quite pure it may be kept unchanged, but, in presence of impurities, especially of sulphuric acid, it soon becomes an opaque white mass of *metachloral*, which is insoluble in water, alcohol, and ether. This is probably formed by the condensation of three molecules of chloral, into which it is reconverted at 180° C. It will be remembered that aldehyd is liable to a similar polymerisation. Chloral also resembles aldehyd in forming crystalline compounds with hydrosodium sulphite, and in giving a mirror of silver with the ammonio-nitrate. With ammonia, it forms $CCl_3.C(NH_2.OH)H$, corresponding to aldehyd-ammonia. Zinc and HCl substitute H_3 for the Cl_3 in chloral, converting it into aldehyd. Nitric acid oxidises it to trichloracetic acid, $CCl_3.CO_2H$. Potash decomposes it easily; $CCl_3.COH + KOH = CCl_3H$, *chloroform*, $+ H.CO.OK$, *potassium formate*. Chloral is formed when starch or sugar is distilled with HCl and MnO_2.

Chloral hydrate, $CCl_3.C(OH)_2H$, produced by the combination of chloral with water, forms prismatic crystals, which are very soluble in water and alcohol, and have the odour of chloral. It fuses at about 50° C., and boils at 97°, but is dissociated into chloral and steam, which recombine on cooling. Chloral hydrate is employed medicinally for procuring sleep.

Chloral alcoholate, $CCl_3.C.OH.OC_2H_5.H$, is formed when chloral is dissolved in alcohol. It forms crystals like the hydrate, but is rather less soluble in water.

Bromal, obtained by the action of bromine on alcohol, is very similar to chloral.

Croton-chloral, or *butyl-chloral*, $C_3H_4Cl_3.COH$, has the same relation to butyl aldehyd, $C_3H_7.COH$, that chloral has to ethyl-aldehyd, and is prepared by substituting aldehyd for alcohol in the preparation of chloral, when croton-aldehyd is first produced, and is converted into butyl chloral ; (1) $2CH_3COH = CH_3.C_2H_2.COH$, *croton-aldehyd*, $+ H_2O$; (2) $CH_3.C_2H_2.COH + 2Cl_2 = C_3H_4Cl_3.COH + HCl$.

Croton-chloral is an oily liquid of pungent odour, sp. gr. 1·4, and boiling-point, 164° C. It combines with water to form a hydrate which dissolves in hot water, and crystallises, on cooling, in plates which have a very irritating odour. It has been used in medicine.

Chloroform, or *tri-chloromethane*, $CHCl_3$, is prepared by distilling 1 part of alcohol (sp. gr. .834) with 10 parts of chloride of lime and 40 parts of water, at 65° C., until about $1\frac{1}{2}$ part has passed over ; the distilled liquid, consisting chiefly of water and chloroform, separates into two layers ; the chloroform, which is at the bottom, is drawn off, shaken with strong sulphuric acid to remove some impurities, and when it has risen to the surface it is separated and purified by distillation until it boils regularly at 61° C. (142° F.).

The action of chloride of lime on alcohol has not been clearly explained; it might be expected that chloral would be formed at first by the oxidising and chlorinating actions, and that this would be converted into chloroform and calcium formate by the strongly alkaline calcium hydrate produced from chloride of lime by the action of water (see *Chloral*), but much CO_2 is given off, causing frothing during the distillation. Probably the chloroform is produced by some such reaction as the following—

$$3C_2H_6O + 8Ca(OCl)_2 = 2CHCl_3 + 8H_2O + CO_2 + 5CaCl_2 + 3CaCO_3.$$

Pure chloroform is more easily prepared by decomposing chloral hydrate with potash or soda.

Chloroform is a very fragrant liquid, of sp. gr. 1.53, and boiling-point 61° C. It is very useful in the laboratory as a solvent, and is much used for extracting strychnine and other alkaloids from aqueous solutions. It is also one of the best solvents for caoutchouc. Chloroform is very slightly soluble in water, and gives it a sweet taste. Alcohol dissolves it in all proportions, and it is nearly as soluble in ether. Strong sulphuric acid does not affect it, and is not coloured by pure chloroform. Aqueous solution of potash does not decompose it, but the alcoholic solution converts it into potassium chloride and potassium formate; $CHCl_3 + 4KOH = 3KCl + HCO.OK + 2HOH$. If Dutch liquid ($C_2H_4Cl_2$) be present as an impurity in the chloroform, gaseous chlorethylene (C_2H_3Cl) is evolved. When heated with alcoholic potash and anilin, it yields phenyl-carbamine (p. 620); the powerful odour of which renders this a delicate test for chloroform. Heated with alcoholic solution of ammonia, in a sealed tube to 180° C., it gives ammonium chloride and cyanide; $CHCl_3 + 5NH_3 = 3NH_4Cl + NH_4.CN$. When heated with potassium-amalgam, chloroform evolves acetylene; $2CHCl_3 + 3K_2 = C_2H_2 + 6KCl$. That chloroform is really a substitution-derivative from methane, is shown by its conversion into that gas when dissolved in alcohol and heated with zinc-dust, by the formation of tetrachloro-methane, CCl_4, by the action of chlorine (in presence of iodine) upon chloroform, and by that of dichloro-methane, CH_2Cl_2, by the action of zinc and sulphuric acid.

When chloroform is heated with sodium ethylate, it is converted into *ortho-formic ether;* $CHCl_3 + 3NaOC_2H_5 = 3NaCl + CH(OC_2H_5)_3$.

Bromoform, $CHBr_3$, is produced when bromine is added to an alcoholic solution of potash. It has a general resemblance to chloroform. Crude bromine sometimes contains bromoform.

Iodoform, CHI_3, or *tri-iodo-methane*, is a product of the action of iodine upon alcohol in an alkaline solution, the immediate agent being probably a hypo-iodite, whilst chloroform is produced by a hypo-chlorite. To prepare it, dissolve 32 parts of potassium carbonate in 80 parts of water, add 16 parts of alcohol of 95 per cent. and 32 parts of iodine; heat gently till the colour of the iodine has disappeared, when iodoform will be deposited on cooling. Much of the iodine has been converted into KI; to recover this, the filtrate from the iodoform is mixed with 20 parts of HCl and 2.5 parts of potassium dichromate, which liberates the iodine. The liquid is neutralised with potassium carbonate, and 32 parts more of that salt are added, together with 6 parts of iodine and 16 of alcohol; the operations of heating and cooling are then repeated.

Iodoform is deposited in yellow shining hexagonal plates, smelling of saffron. It fuses at about 115° C., and may be sublimed with slight decomposition. It is insoluble in water, but soluble in alcohol and ether. When boiled with potash, it is partly volatilised with the steam, and partly decomposed, yielding potassium iodide and formate. The production of iodoform is a very delicate test for alcohol (p. 489), but many other substances also yield it. Iodoform is used in medicine and surgery.

Chloriodoform, $CHICl_2$, is obtained by distilling iodoform with $HgCl_2$. It is a yellow liquid, boiling at 131° C. The corresponding bromine compound has been prepared.

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⁂ *The names of minerals are printed in italics.*

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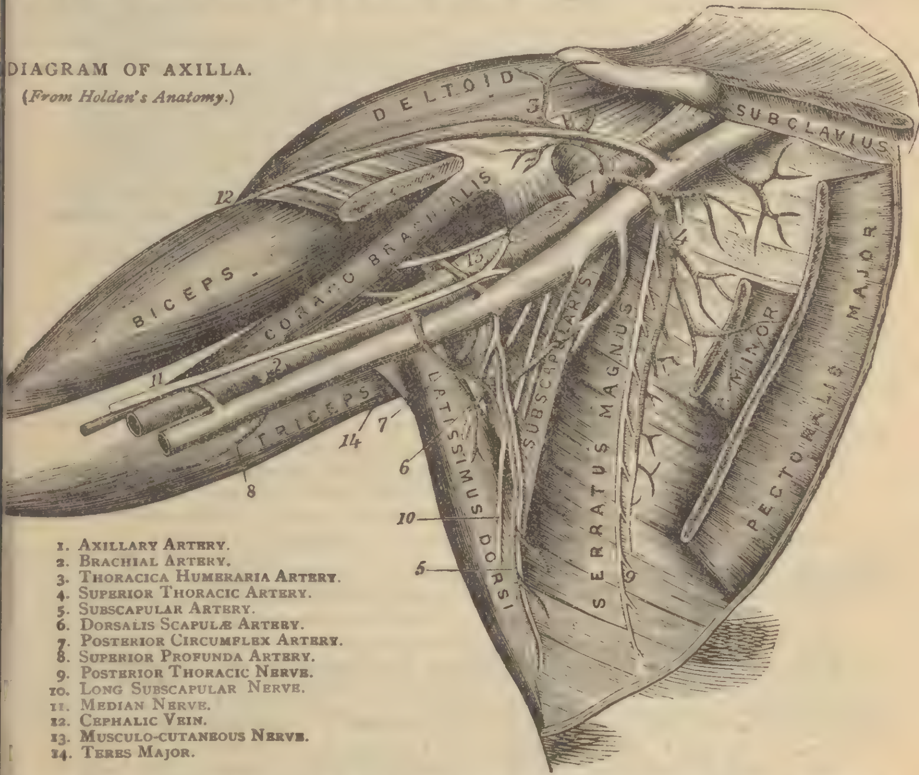

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